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Charge carrier mobility in poly(p-phenylenevinylene) studied by the time-of-flight technique

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The charge carrier transport in poly(p-phenylenevinylene) (PPV) is investigated by the time-of-flight technique. Mobilities of positive carriers in PPV are determined and the dispersive character of transport is established. The dispersion parameters are analyzed in the frame of a multiple trapping model. The drift mobility of the positive carriers is in the range of 10^{-5} cm²/V s at room temperature for an electric field of 10^5 V/cm and increases with increasing field and temperature. The mobility shows thermally activated behavior with an activation energy of about 0.75 eV at zero field. It is shown that the experimental results can be interpreted by polaron transport. © 1997 American Institute of Physics. [S0003-6951(97)03944-2]

There is increasing interest in conjugated polymers such as poly(p-phenylenevinylene) (PPV) and its derivatives as luminescent materials.^{1,2} Despite the great progress in the development of light emitting diodes (LEDs) the nature of excitations and transport in PPV and its derivatives are still under discussion.² Thus, the investigation of charge carrier mobilities in PPV would be helpful not only for further improvement of LEDs based on conjugated polymers but also for a deeper understanding of elementary excitations in PPV.

Transport properties were studied by the time-of-flight technique (TOF) for two soluble PPV derivatives.^{3,4} However, up to now the drift mobility could not be directly measured in unsubstituted PPV because of a featureless photocurrent decay. From their data Meyer *et al.* could only estimate an upper limit for the hole mobility of 10^{-8} cm²/V s.⁴ Therefore, our work is aimed primarily at the direct determination of the drift mobility of carriers in PPV by TOF and the investigation of the temperature and field dependent characteristics of the mobility.

Since the TOF technique is well suited to investigate the nature of charge carrier transport, we address the question on the involvement of polarons in the transport. While Gailberger and Bässler have found that polaronic effects are negligible for dispersive transport in a phenyl-substituted PPV (PPPV),³ the importance of tunneling of charge carriers into polaron levels has been suggested for contact injection into polymer LEDs.⁵ Experimental evidence for the existence of bipolaron states in PPV at 0.6 and 1.6 eV was obtained from photoinduced absorption spectra.⁶

PPV films were prepared on indium–tin–oxide (ITO) coated glass substrates by thermal conversion of a soluble precursor as described in Ref. 7. The elimination products HCl and tetrahydrothiophene (THT) can undergo chemical reactions with the ITO substrate leading to doping of PPV by InCl₃ (Ref. 8) and to the formation of defects at the ITO/PPV

interface, which becomes more important the thicker the converting PPV film is. For film thicknesses exceeding about 500 nm a partial destruction of the ITO substrate could already be observed. To avoid the enrichment of leaving groups in the film and thus reduce their reaction with the ITO we subsequently casted and converted several PPV layers of about 200 nm thickness each. Additionally, due to the high optical absorption coefficient the total thickness of the PPV layers could be chosen rather thin as compared to usual TOF measurements on polymers, and ranged between 0.7 and 1.5 μm. TOF measurements were performed on ITO/PPV/Al sandwich structures with a conventional experimental setup.⁹ The excess carriers were generated by illumination with pulses of a N₂ laser (wavelength 337 nm, pulse duration 0.3 ns) through the semitransparent Al electrode, which forms a non-injecting contact for holes with PPV. The excitation intensity was chosen well below the level for space charge distortion of the applied electric field. The electric field was applied for a duration between 1 and 10 ms and the delay time of the laser pulse was 0.1 ms.

The mobility of holes in PPV can be obtained from the photocurrent transients as depicted in figure 1. The shape of the curves is typical for dispersive transport in organic polymers. The change of slopes in the double logarithmic plot originates from the passage of carriers through the sample and determines the transit time t_{tr} . The drift mobility can be calculated as $\mu = L/t_{tr}F$, where L is the thickness of the sample and F the applied electric field. TOF measurements were performed in the temperature range between 275 and 320 K and applied electric fields between 6.4×10^4 and 4×10^5 V/cm. The mobility obtained follows an Arrhenius law with a field dependent activation energy as shown in figure 2. The activation energy E_A decreases with increasing field and the extrapolation gives a rough estimate of $E_A^{(0)} = 0.75$ eV at zero field (inset in figure 2). This value is in the same range as the measured activation energy of the dc conductivity of PPV ($E_A^{dc} \approx 0.6$ eV).¹⁰ The field dependence of the drift mobility at $T = 277$ K is presented in figure 3. The drift mobility

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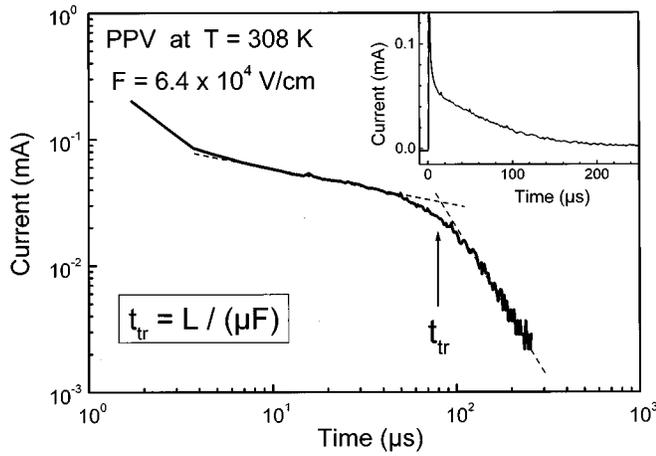


FIG. 1. Photocurrent transient of PPV at a temperature $T=308$ K and an electric field $F=6.4 \times 10^4$ V/cm in a linear plot (inset) and in a double logarithmic plot. The sample thickness was $0.7 \mu\text{m}$.

of the positive charge carriers increases with increasing electric field. In both representations linear regressions yield satisfactory fits to the experimental data. It is therefore hard to distinguish whether a polaron hopping model¹¹ [case (a)] or a Poole-Frenkel mechanism [case (b)] is more appropriate to describe the measured mobility of PPV.

Our data clearly show that due to our improved film preparation technique it is possible to obtain hole mobilities in PPV directly by TOF. The values of the drift mobility are in good agreement with those estimated from space-charge limited currents¹² but they are considerably larger than the ones derived from the delay time of pulsed electroluminescence.¹³ Compared to the soluble PPV derivatives, the mobility data of PPV are of the same order of magnitude as that of PPPV³ and only about a factor of 10 lower than in diphenoxyphenyl-PPV (DPOP-PPV).⁴

Photocurrent transients have been analyzed further in the frame of the stochastic theory of dispersive transport. A multiple trapping model yields different power law dependencies of the photocurrent transient $I(t)$ before and after the transit time t_{tr} .¹⁴

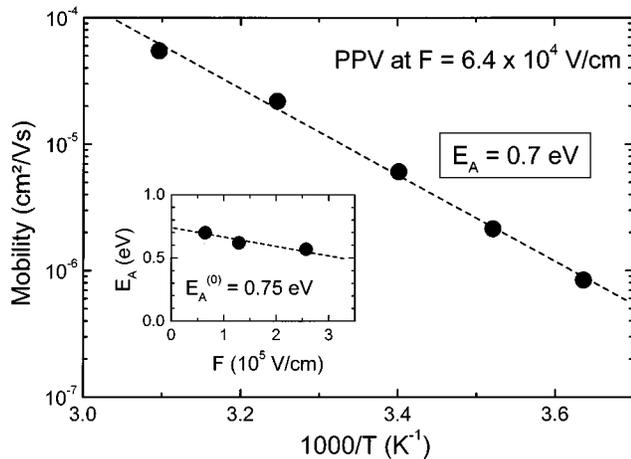


FIG. 2. Temperature dependence of the drift mobility in PPV at $F=6.4 \times 10^4$ V/cm in an Arrhenius representation. The inset shows the field dependent activation energy of the drift mobility with an extrapolation to zero field.

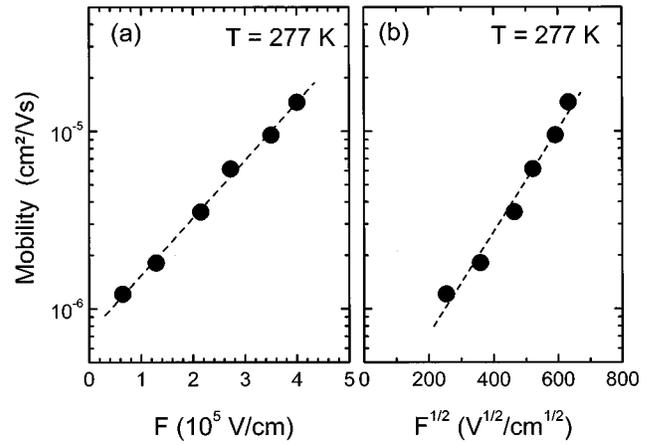


FIG. 3. Dependence of the drift mobility in PPV at $T=277$ K on the electric field (a) (polaron hopping model) and on the square root of the electric field (b) (Poole-Frenkel model).

$$I(t) \propto \begin{cases} t^{-(1-\alpha_i)}, & t < t_{tr} \\ t^{-(1+\alpha_f)}, & t > t_{tr} \end{cases}, \quad (1)$$

where α_i and α_f are the dispersion parameters. The values of the dispersion parameters range between 0 and 1 and decrease with increasing dispersion. In the case of dispersive transport controlled by multiple trapping on localized states with an exponential energy distribution $N(E)=N_0 \cdot \exp(-E/E_0)$ it was shown that $\alpha_i=\alpha_f \equiv \alpha$, with $\alpha = kT/E_0$.¹⁵ In figure 4 dispersion parameters α_i and α_f for PPV at 323 and 273 K at $F=6.4 \times 10^4$ V/cm are determined. It is important to note that $\alpha_i \neq \alpha_f$. For all investigated transients $\alpha_i < \alpha_f$ was found. The values of α_i and α_f increase with increasing temperature. The inset of figure 4 shows the temperature dependence of α_i for $F=6.4 \times 10^4$ V/cm. The field dependence of α_i is shown in figure 5 for PPV at 293 K. The value of α_i decreases with increasing field from about 0.7 to 0.45. This implies that the distribution of localized states should decay faster than exponential ones. This is the case, for example, for a Gaussian distribution. The following

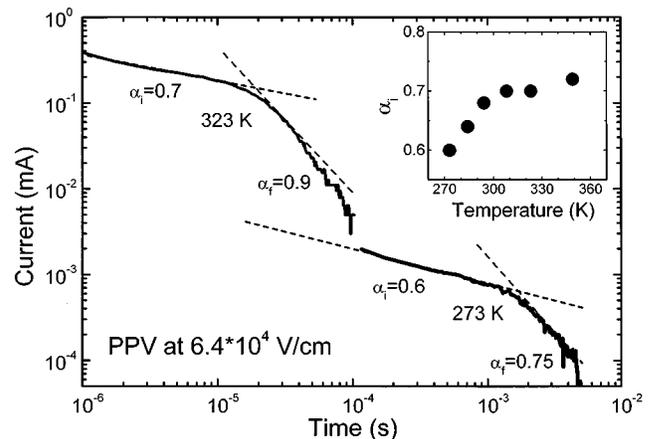


FIG. 4. Photocurrent transients of PPV at 323 and 273 K and at $F=6.4 \times 10^4$ V/cm. The values of α_i and α_f are derived from linear fits. The inset shows the temperature dependence of α_i for $F=6.4 \times 10^4$ V/cm.

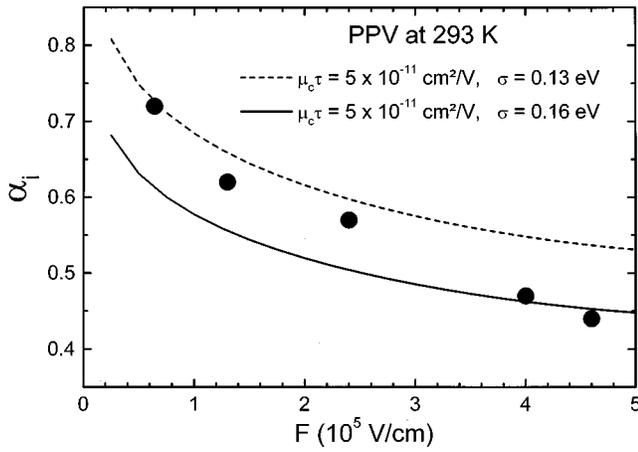


FIG. 5. Field dependence of α_i for PPV at $T=293$ K (circles). The dashed and solid lines show the theoretical field dependence of α_i obtained from equation (3) for different values of σ .

Gaussian-like distribution of localized states has been analyzed from the point of view of dispersive transport:¹⁶

$$N(\varepsilon) = \frac{2N_t}{\sigma} \cdot \frac{\varepsilon}{\sigma} \cdot \exp\left[-\left(\frac{\varepsilon - \varepsilon_t}{\sigma}\right)^2\right], \quad (2)$$

where N_t , E_t and σ are the number, the energy and the width of the distribution, respectively. The analytical expressions for α_i and α_f are given by

$$\alpha_{if} = \frac{2kT}{\sigma} \cdot \left(\ln \frac{L}{\sqrt{2}\mu_c\tau F}\right)^{1/2} \cdot \left(1 \pm \frac{1}{2} \ln \frac{L}{\sqrt{2}\mu_c\tau F}\right), \quad (3)$$

where (+) should be taken for α_i and (-) for α_f . μ_c and τ are carrier mobility and lifetime in the band before trapping, respectively. We remark that analytical solutions for the dispersion parameters could not be obtained in the case of a pure Gaussian distribution of localized states. The parameters $\mu_c\tau$ and σ may be estimated from figure 5 by using equation (3). We obtain for $\mu_c\tau$ a value in the order of 5×10^{-11} cm²/V and for σ a value between 0.13 and 0.16 eV. The activation energy of the mobility in the case of distribution (2) is given by $E_A = E_t + \sigma^2/2kT$, while the energy at the maximum of the distribution is $E_{\max} = E_t + \sigma/\sqrt{2}$. The value of E_t at a given temperature can be obtained from the measured activation energy of the mobility and the estimated value of σ . Then the distribution of the localized states has its maximum E_{\max} at an energy ranging between 0.35 and 0.5 eV.

The results of our TOF investigations can be interpreted in the frame of polaron transport in PPV. The conductivity of systems containing polarons and bipolarons was investigated in¹⁷. In that model polarons contribute directly to the transport via hopping and bipolarons indirectly as sources for polarons. A very similar approach can be found in Ref. 10. The measured activation energy of the drift mobility is then the sum of the activation energy of polaron hopping and the energy to activate polarons out of bipolaronic states: $E_A = E_P + E_B$. With $E_B = 0.6$ eV from photoinduced absorption⁶ one yields the polaron hopping energy $E_P = 0.15$ eV.

In summary, the temperature and field dependent values of the drift mobility and the dispersion parameters of PPV have been measured directly by TOF. Our results show that the transport characteristics of PPV are not contradictory to the polaronic nature of carriers in PPV.

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