Effect of Spatial Irregularities on the Temperature and Field Dependence of the Mobility in Liquid-Crystalline Conjugated Polymer Films

Simon J. Martin, Agapi Kambili, Alison B. Walker*

Department of Physics, University of Bath, Claverton Down, Bath BA2 7AY, UK

Summary: We have performed simulations of time-of-flight measurements via the Monte Carlo approach for films made of conjugated polymers in the liquid-crystalline phase. In spatially regular films with a distribution of on-site energies the mobility is affected by the interplay between electrostatic and thermal energy. When the width of the on-site energy distribution is comparable to the thermal energy, the mobility increases with temperature at low fields, but shows the opposite behaviour at larger fields. However, when spatial irregularities in the arrangement of the film are introduced, the mobility is enhanced at all temperatures, as the electrostatic energy plays less of a role in charge transport than thermal activation over energy barriers.

Keywords: charge transport; conjugated polymers; light-emitting diodes; Monte-Carlo simulation; spatial arrangement

Introduction

Conjugated polymers[1] have promising applications to solar cells and photodetectors[2-4]. In polymer light-emitting diodes[5] detailed investigation of the materials has resulted in rapid progress[6]. To commercialise polymer devices, high efficiencies, brightness, and carrier lifetimes are required[7]. It is, therefore, essential to fully understand the fundamental physics of electrical transport through conjugated polymers; for a recent review, see[8].

Previous theoretical studies have dealt with strongly disordered organic materials, with charge transport mainly attributed to hopping[9-11], and low carrier mobilities that depend strongly on temperature and electric field. However, large carrier mobilities are generally required. Recent measurements on aligned polymer films[12-14] have demonstrated enhanced carrier mobilities, varying only weakly with the electric field. To our knowledge, this weak field dependence has not yet been explained.

 DOI: 10.1002/masy.200450828

This realization has motivated us to investigate the transport properties of liquid-crystalline conjugated polymer films with the chains nematically aligned perpendicular to the direction of transport. In a previous work[15] we looked into the character of transport through such polymer films, and we showed that it is possible to obtain non-dispersive transport, in agreement with time-of-flight experiments conducted on liquid-crystalline polyfluorene (PFO) films[12, 13]. In the present work the interplay between electric field and temperature on the transport characteristics is examined in combination with the competing effect of spatial irregularities in the arrangement of the polymer chains.

The Model

In order to investigate the transport properties of liquid-crystalline polymer films, we have performed numerical simulations of the time-of-flight technique. The film is composed of conjugated polymer chains of length L = 100 nm which are nematically aligned perpendicular to the direction of the electric field, chosen as the x direction, with periodic boundary conditions applied along the other two directions. Based on the extended backbone conjugation of liquid-crystalline polymers, such as PFO, that makes them stiff, and on bond vibrations being of very high frequency and low amplitude, we have assumed that the polymer chains can be described as rigid rods. The thickness of the film in the direction of transport has been taken equal to d = 1 μm.

Hopping motion of the charge carriers under the influence of the electric field is assumed, which in general can be either intra- or inter-chain, and is described by a simple Monte Carlo model. The charges are taken to be negative here, but positive charge can be equally treated. At the start of the simulation, the charges are placed on the chains adjacent to the injecting electrode. The unnormalized probability of hopping between two sites i and j is equal to

$$p_{ij} = \gamma \exp\left(-\frac{\varepsilon_j - \varepsilon_i - e\vec{E}\vec{r}_{ij}}{k_B T}\right) \qquad (1)$$

$\vec{E}$ is the electric field, $\vec{r}_{ij}$ is the relative position vector, k_B is the Boltzmann factor, and T is the temperature. γ denotes the electronic wavefunction overlap, and in the following we have considered only nearest-neighbouring hopping within a cut-off distance equal to 10 Å. The on-site energies ε_i are taken from a Gaussian distribution whose width σ determines the degree of

energetic disorder present in the film. Since liquid-crystalline conjugated polymers are generally characterized by a high degree of chemical regularity, a small value of σ is adequate. Here, we have taken $\sigma/\kappa_B T = \alpha$, with α being of the order of 1, and $T = 300$ K.

Results and Discussion

First, we examine the case of equidistant arrangement of the chains, with all inter-chain distances equal to 10 Å (spatially regular case). In Figure 1 we present a current transient from our numerical simulations for electric field $E = 3 \times 10^5$ V/cm at room temperature, and for disorder $\alpha = 1$. The calculated current exhibits the typical behaviour of a time-of-flight signal, with a plateau followed by a decaying tail, indicative of non-dispersive transport[16]. From the current transient we extract the transit time t_T by using the current integration mode, which determines the transit time as the point at which the current has fallen to half its value in the plateau region.

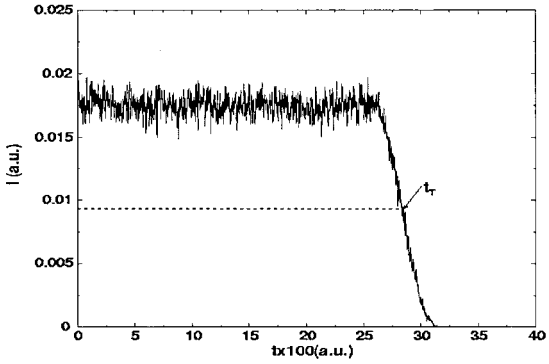

Figure 1. Current transient for $\alpha = 1$, $E = 3 \times 10^5$ V/cm, and $T = 300$ K, for regularly spaced chains. The transit time t_T is indicated by the arrow.

By identifying the transit times from the current transients for various values of the external electric field and for different temperatures, we have calculated the mobility via the relation $\mu = d/(Et_T)$. Figure 2 shows $\ln\mu$ as a function of $E^{1/2}$ for temperatures in the range from 100 K to 350 K. The left panel corresponds to $\alpha = 0.5$, and the right panel to $\alpha = 1$. For $\alpha = 0.5$, as the field increases for a given temperature, $\ln \mu$ decreases, since at large fields the electrostatic energy forces the charge carriers to follow shorter paths, causing the transit time to saturate. $\ln \mu$ decreases with temperature for all values of E, as seen in crystalline semiconductors. On the other

hand, when $\alpha = 1$, at a given temperature, ln μ always increases with the electric field. The effect is more pronounced at small T, as the thermal energy is not sufficient to enable the carriers to surmount the energy barriers. At a given field, there is a crossover between the behaviour at low fields, where ln μ increases with temperature, and the behaviour at high fields, where the mobility decreases with T. A similar crossover has also been observed in other types of polymers within a Master equation approach[17]. However, in that case the crossover appears to occur at the same field for all temperatures considered. At room temperature, our mobility increases by a factor of 1.2, in approximate agreement with experimental data[12].

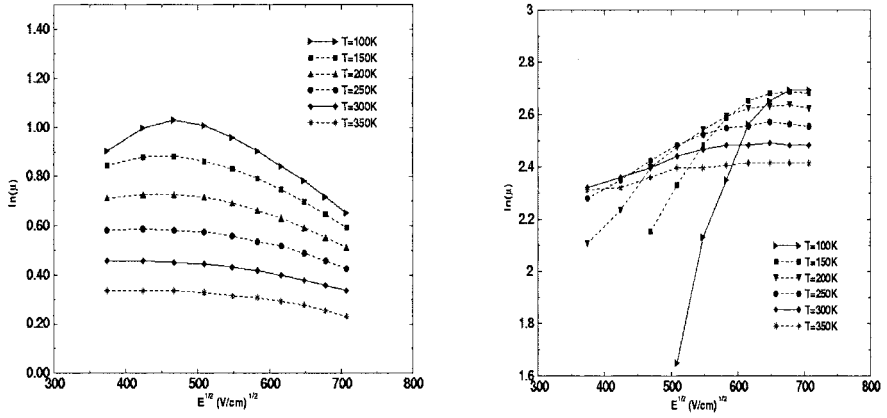

Figure 2. The mobility μ (arbitrary units) as a function of $E^{1/2}$ and for various temperatures, for regularly spaced chains. The left graph is for energetic disorder $\alpha = 0.5$, and the right graph for $\alpha = 1$.

The observed crossover with temperature does not appear in strongly disordered polymeric materials, in which the mobility always increases with T [6]. In Figure 3 we show ln μ versus $E^{1/2}$ for various temperatures, but for energetic disorder $\alpha = 1.5$. The crossover that was previously seen now appears only in a small range of the field values, in particular at large E, and around room temperature. Thus, as the energetic disorder increases, the thermal energy aids the motion of the charge carriers towards the collecting electrode.

Figure 4 shows ln μ as a function of $E^{1/2}$ and T, for $\alpha = 0.5$ (left) and $\alpha = 1$ (right), respectively, for a film in which the inter-chain distances vary randomly between 7 Å and 13 Å (irregularly spaced chains). Hopping is only allowed to nearest neighbours within the same cut-off distance as

before. For small α, ln μ behaves in the same way as for the case of regular chain spacing in that at constant temperature it decreases with the field and for a fixed field it is lowered with temperature. For $\alpha = 1$, the mobility is enhanced with temperature for all values of the electric field, as was shown in recent measurements of PFO films[18]. This behaviour resembles that of strongly disordered polymer films[6]. In our case the increase in ln μ with temperature arises from the spatial irregularities in the arrangement of the chains within the film, since the distribution in the relative position vector leads to variations in the electrostatic energy, and thermal activation dominates. In all cases, however, μ varies only weakly with the electric field.

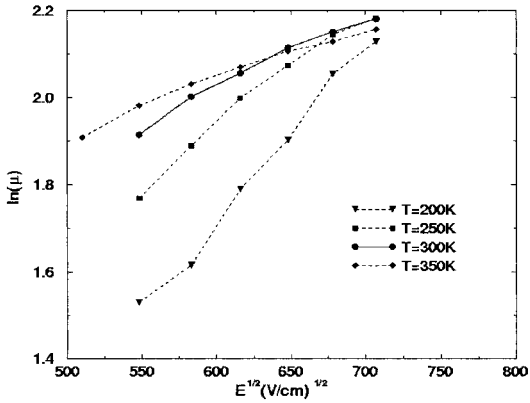

Figure 3. The mobility μ (arbitrary units) as a function of $E^{1/2}$ and for various temperatures, for regularly spaced chains and energetic disorder $\alpha = 1.5$

Summary

In this paper, we have presented calculations of the mobility of charge carriers through liquid-crystalline polymer films. By employing the Monte Carlo technique, we have investigated the electric field and temperature dependence of the mobility for films with energetic disorder comparable to the thermal energy. At room temperature the mobility varies only weakly with the electric field, and for energetic disorder parameter $\alpha = 1$, our predictions are in qualitative agreement with experimental data on PFO films[12]. For regularly spaced chains and for $\alpha = 1$, the mobility decreases with temperature for small fields and increases with T for larger fields. However, for random inter-chain distances the mobility increases with temperature, in agreement with recent experimental findings[18].

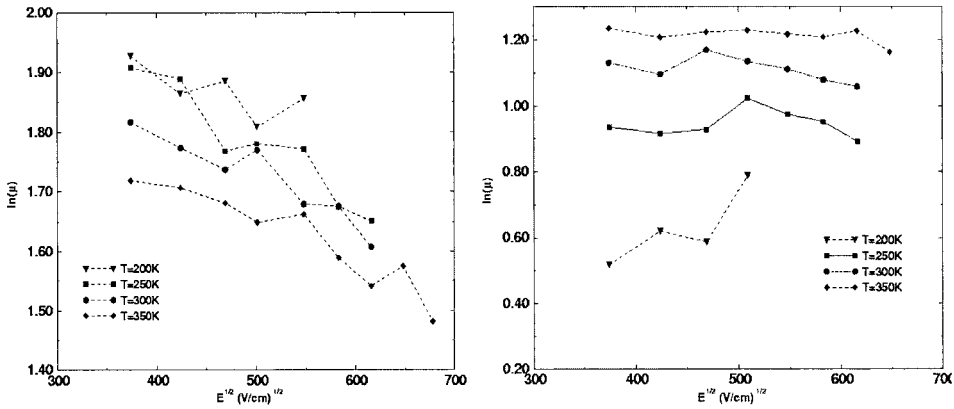

Figure 4. The mobility μ (arbitrary units) as a function of $E^{1/2}$ and for various temperatures, for irregularly spaced chains. The left graph is for energetic disorder $\alpha = 0.5$, and the right graph for $\alpha = 1$.

[1] M. Pope and C. E. Swenberg, "*Electronic Processes in Organic Crystals and Polymers*" Oxford University Press **1999**

[2] P. Gattinger, H. Rengel, D. Neher, *J. Appl. Phys.***1998**, *84*, 3731

[3] P. Peumans, V. Bulović, S. R. Forrest, *Appl. Phys. Lett.* **2000**, *76*, 2650

[4] F. Zhang, M. Svensson, M. R. Andersson, M. Maggini, S. Bucella, E. Menna, O. Inganäs, *Adv. Mater.* **2001**, *13*, 1871

[5] J. H. Burroughes, D. D. C. Bradley, A. R. Brown, R. N. Marks, K. Mackay, R. H. Friend, P. L. Burn, A. B. Holmes, *Nature* **1990**, *347*, 359

[6] G. Hadziioannou and P. F. van Hutten, "*Semiconducting Polymers, Chemistry, Physics and Engineering*", Wiley-VCH, Weinheim, 2000

[7] R. H. Friend, R. W. Gymer, A. B. Holmes, J. H. Burroughes, R. N. Marks, C. Taliani, D. D. C. Bradley, D. A. Dos Santos, J. L. Brédas, M. Lögdlund, W. R. Salaneck, *Nature* **1999**, *397*, 121

[8] A. B. Walker, A. Kambili, S. J. Martin, to be published in *J. Phys.: Condens. Matter.* **2002**

[9] H. Bässler, *Phys. Status Solidi* **1993**, *175*, 15

[10] S. V. Novikov, D. H. Dunlap, V. M. Kenkre, P. E. Parris, A. V. Vannikov, *Phys. Rev. Lett.* **1998**, *81*, 4472

[11] S. V. Rakhmanova, E. M. Conwell, *Synth. Met.* **2001**, *116*, 389

[12] M. Redecker, D. D. C. Bradley, M. Inbasekaran, E. P. Woo, *Appl. Phys. Lett.* **1998**, *73*, 1565

[13] M. Redecker, D. D. C. Bradley, M. Inbasekaran, E. P. Woo, *Appl. Phys. Lett.* **1999**, *74*, 1400

[14] H. C. F. Martens, O. Hilt, H. B. Brom, P. W. M. Blom, J. N. Huiberts, *Phys. Rev. Lett.* **2001**, *87*, 086601

[15] A. Kambili, A. B. Walker, *Phys. Rev. B* **2001**, *63*, 012201

[16] J. C. Scott, B. A. Jones, L. T. Pautmeier, *Mol. Cryst.* **1994**, *253*, 183

[17] Z. G. Yu, D. L. Smith, A. Saxena, R. L. Martin, A. R. Bishop, *Phys. Rev. B* **2001**, *63*, 085202

[18] D. Poplavskyy, T. Kreouzis, A. J. Campbell, J. Nelson, D. D. C. Bradley, Paper P1.4, *Materials Research Society, 2002 Spring Meeting, MRS Proceedings* (Eds: G. E. Jabbour, N. S. Sariciftci, S. T. Lee, S. Carter, J. Kido) **2002**, 725