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High electric field effect on hopping conduction in molecularly doped polymer systems

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Abstract

Time of flight mobility measurements were carried out in thin films of solid solution of amorphous polycarbonate molecularly doped with *N*-isopropylcarbazole by using electron beam bombardment. The dependence of the hole drift mobility (μ) with the applied electric field was analysed in the scope of both, the Poole–Frenkel emission model and a density of state model which does not invoke the existence of charged traps. The experimental results were in just agreement with the Poole–Frenkel model through the whole range of the electric field used during the experiment; however, the agreement with the density of state model was evident only at fields greater than 0.8 MV/cm. To justify this behaviour, an additional consideration in the Poole–Frenkel model was proposed which allowed to conclude, that the circumstantial agreement with the density of state model at the highest range of electric field results from the fact that the traps become inoperative at this range of field, and not because the traps were really absent. © 1999 Elsevier Science Ltd. All rights reserved.

Keywords: Drift mobility; Traps; Poole–Frenkel

1. Introduction

Molecularly doped polymers represent a genuine molecular systems where, the charge transport is carried out by a hopping mechanism between the dopant molecules which act like hopping sites [1]. This mechanism can be visualised using a two centres model [2] where the carriers hop from one centre to the other. If the centres are charged when empty, the hop ocurrs above a potential barrier. Different factors such as temperature (T), separation between centres (R), distribution of hopping energy and electric field (F) would govern this type of charge transport by increasing the hopping probability. By considering these factors one can obtain the corresponding conduction parameters. In this context, we will focus attention on the effect of application of strong electric fields. Indeed, experimental results were reported in the literature, on drift mobility (μ) and dc electrical conductivity, which appear to be consistent with the emission mechanism of Poole–Frenkel [3–5]. In this model, the application of a strong enough external electric field modifies the potential barrier profile of the trap to make it easy for the trapped carrier to be liberated from the trap without thermal activation. The field lowers the height of the potential barrier by $\beta F^{1/2}$, where β is the coefficient of Poole–Frenkel given by $(e^3/\pi\epsilon\epsilon_0)^{-1/2}$, ϵ is the high-frequency dielectric constant, ϵ_0 the free space permittivity and e the electron charge. The reduction of the potential wall (ΔE), in an unidimensional picture [6] is given by:

$$\Delta E = (\Delta E)_0 - \beta F^{1/2}, \tag{1}$$

where, $(\Delta E)_0$ is maximum in the absence of an applied electric field. The corresponding drift mobility will therefore be increased by this factor following the relation:

$$\mu(F) \propto \exp[\beta F^{1/2}/kT]. \tag{2}$$

Plots of Eq. (2) in the representation ln μ vs. $F^{1/2}$, at a given temperature, would be straight lines from whose slopes one can estimate the value of β. Nevertheless, a computer simulation carried out on a trap free molecular system, where hopping energy is subject to a gaussian distribution [7], gives as a result a drift mobility linearly dependent on the electric field, obeying, at a given temperature, the relation:

$$\mu(F) \propto \exp[F/F_0], \tag{3}$$

where, F_0 is the characteristic electric field related to the width of the distribution. A plot of Eq. (3) in a ln μ vs. F representation would be a straight line. In this contribution we are reporting hole drift mobility in thin films of polycarbonate of bisphenol A (PC) molecularly doped

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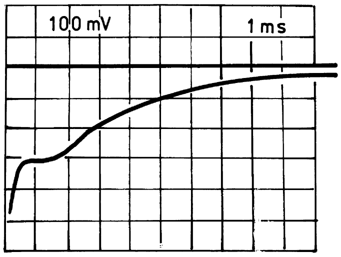

Fig. 1. Typical hole transit signal for a specimen of polycarbonate doped with 10% of *N*-isopropylcarbazole, 12 μm thick for a field of 0.82 MV/cm at RT.

with *N*-isopropylcarbazole (NIPK), to establish the range of applicability of both models.

2. Experimental details

Polycarbonate of bisphenol A (Aldrich Chemical Co.) low molecular weight and density 1.20 g/cm^3 was purified by dissolving in chloroform and precipitating with isopropylalcohol (analar). *N*-isopropylcarbazole (Estman Co.) was purified by recrystallisation from methanol. Weighted amounts of both materials were dissolved in a common solvent (dichloromethane) and stirred to ensure a uniform mixture. The actual content of NIPK in each film is stated in percentage by weight, actually 0.5 g of PC were dissolved in dichloromethane and different percentages between 10% and 60% of NIPK were incorporated into the solution. Films typically 10–12 μm thick, were deposited onto aluminized glass substrates by spreading the solution under a sliding blade. Once the residual solvent was evaporated, the films were top-coated with an aluminium electrode forming samples with a structure Al–PC/NIPK–Al. At the end of the experiment the thickness of the films were determined by a tallysurf instrument. The Drift mobility was obtained by time-of-flight measurements using electron beam bombardment [8,9]. In a typical experiment, the bombardment dose was kept to 10 pC pulse/shot to ensure space charge free transit and minimise damage to the samples. An interval between shots of about 10 s was allowed to avoid any polarization effect caused by previous electron pulses. Normally, a single pulse of electrons, 4 μs wide, was applied to the specimen within a few seconds after the bias voltage which was removed once the current transient had been recorded at room temperature. Charge transit was only observed when the bombarded electrode was positively biased, indicating an electronic transport by holes [10]. Under these experimental conditions, accumulation of space charge was negligible so that hole drift mobility could be obtained from the relation:

$$\mu = L^2/Vt_t, \tag{4}$$

where, L is the thickness of the sample, V the bias voltage and t_t the hole transit time.

3. Experimental results

Fig. 1 shows the hole transit signal for a typical specimen of polycarbonate doped with 10% by weight of *N*-isopropylcarbazole, 12 μm thick, for a field of 0.82 MV/cm at room temperature. The profile shows a well defined shoulder from which the transit time is directly estimated. Similar profiles were obtained for all the samples under bombardment.

Fig. 2 depicts the behaviour of the hole drift mobility with electric field in a ln μ vs. $F^{1/2}$ plot for two different contents of NIPK. A straight line can be fitted over the entire range of the electric field, obeying the Poole–Frenkel mechanism given by Eq. (2).

Fig. 3 shows the same data as Fig. 2 in an ln μ vs. F representation. For samples with a high content of NIPK,

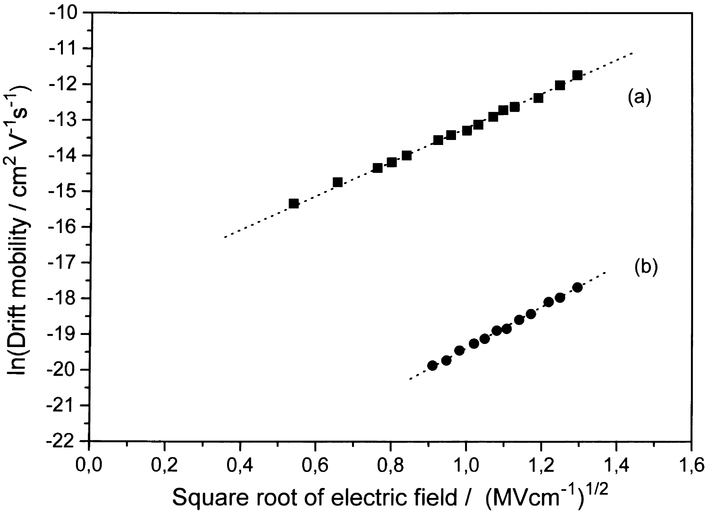

Fig. 2. Dependence of the hole drift mobility with the square root of the electric field at RT, for two different contents of *N*-isopropylcarbazole: (a) 60% by weight and (b) 10% by weight.

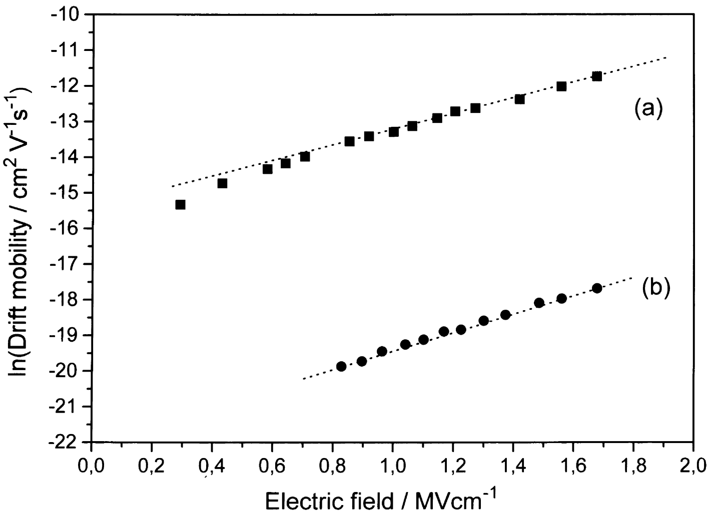

Fig. 3. Dependence of the hole drift mobility with electric field for the same samples as Fig. 2.

60% by weight, (see Fig. 3(a)), a straight line can be fitted only for $F > 0.8$ MV/cm. This behaviour appears more evident in specimens doped with 10% by weight of NIPK where greater electric fields are required to observe definable transit time (see Fig. 3(b)). A similar linear behaviour at the same range of electric field can be observed in other molecularly doped polymer systems [11–14].

4. Discussion of results

It is known that Eq. (3) is based on the assumption that the existence of charged traps have not been invoked [12]. However, it is difficult to imagine an amorphous polymer film without the presence of charged localised states. Under these circumstances, the fitting of Eq. (3) to our experimental observation shown in Fig. 3, would be justified by suggesting an additional consideration to the Poole–Frenkel model. If one assumes that the height of the potential barrier does not indefinitely reduce by the application of the electric field, there must exist a maximum value beyond which more reduction is not possible. We have fixed this maximum in the order of kT. We then obtain from Eq. (1):

$$(\Delta E)_0 - \beta F^{1/2} = kT. \tag{5}$$

Fig. 4 illustrates the one-dimensional model of Poole–Frenkel showing the maximum reduction of the potential wall. Using the values $(\Delta E)_0 = 0.35\,\text{eV}$ and $\beta = 0.22\,\text{meV}\,(\text{V/cm})^{-1/2}$ reported by Santos and Hirsch [10]

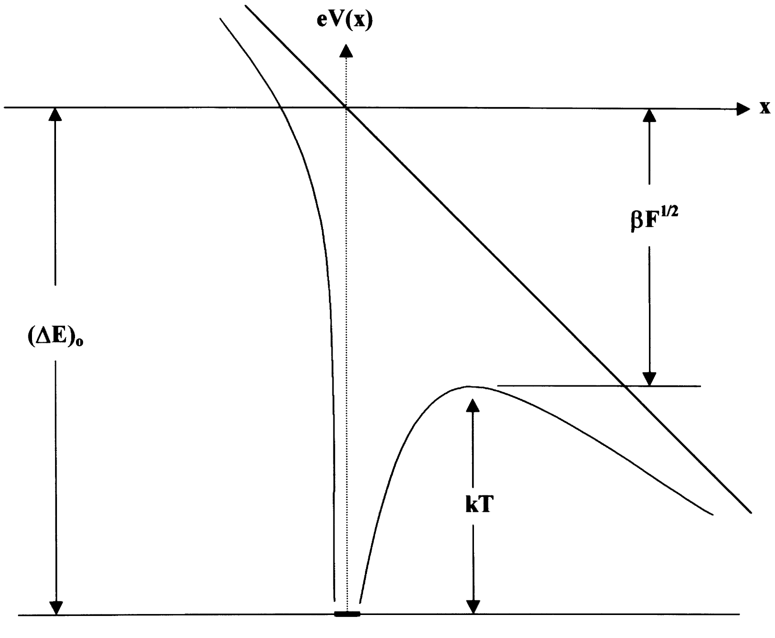

Fig. 4. One dimensional model of Poole–Frenkel showing a reduction of the potential wall of the order of kT.

at room temperature, from Eq. (5) it is estimated $F \approx 2$ MV/cm. It can mean that at fields greater than or of the order of this value the probability for the carrier to be liberated reaches a maximum. At this point we can say that the traps become inoperative and the transport can be described by Eq. (3) and a deviation of the Poole–Frenkel behaviour must be expected. Our experimental results show that the agreement with Eq. (3) occurs for fields greater than 0.8 MV/cm, which is not in concordance with the estimated value of 2 MV/cm. However, our proposal does not lose any essentials of generality owing to this fact as it shows anyway, that the applicability of Eq. (3) is limited to the highest field range. The expected deviation of the Poole–Frenkel behaviour was not observed in our experiment, as measurements at fields beyond 2 MV/cm were not possible without breakdown of the specimens. Consequently Eq. (2) describes our data in the whole range of the electric field used during the experiment ($0.2 \leq F \leq 1.7$ MV/cm).

5. Conclusions

As Eq. (3) was deduced to describe the electronic transport in molecular hopping systems without traps, its applicability to amorphous polymer systems must be considered with care. It is difficult to accept the absence of traps in these materials which, by nature, are rich in ionic species, structural defects owing to the preparation of the films and chemical impurity products of the polymerization processes. The apparent agreement with this equation shown by the experimental results reported in this communication and the other literature (see Refs. [11–14].) is clear to occur at the highest electric field range, which is in qualitative agreement with the argument proposed to describe the behaviour of the coulomb traps in the neighbourhood of 2 MV/cm. In this context, the main conclusion would be that in thin films of amorphous polymers, Eq. (3) describes the dependence of the drift mobility on electric field because the traps become inoperative at the highest range of field, and not because the traps are really absent.

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