Charge Carrier Mobility and Electroluminescence in a Green-Emitting Alternating Block Copolymer with a Methoxy Bi-Substituted Chromophore

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We determine the mobility of positive and negative charge carriers in a soluble green-emitting alternating block copolymer with a methoxy bi-substituted conjugated segment. The negative charge carrier mobility of 6×10^{-11} cm^2/V.s is directly determined using space-charge-limited current analytical expressions. Positive charge carrier transport is also space-charge-limited, with a mobility of 1×10^{-8} cm^2/V.s. The electron trap distribution is exponential, with a characteristic energy of ~0.12 eV. A hole trap with energy ~0.4 eV was observed. This copolymer is used as emissive material in organic light-emitting diodes that present brightness of ~ 900 cd/m^2 at 12.5 V.

I Introduction

As recently analytically demonstrated, the charge carrier mobility is a parameter that plays a crucial role in the performance of pristine-semiconductor- polymers-based light-emitting devices (LEDs) [1]. The distribution of the emissive region of the electroluminescent material in a thin film device is directly controlled by the charge carrier mobilities. In most of the cases the positive charge carrier mobility is up to a few orders of magnitude larger than the negative charge carrier mobility, confining the light emission region to the cathode neighborhood [2]. Wider distributions would be observed when the ratio between the mobility of positive and negative charge carriers tends to one [1].

For LED applications a strength control of the emission wavelength may be interesting. The use of block copolymers permits to control the emission in a way similar to the variation of oligomer molecular mass, but without loss of the useful mechanical properties of polymers. In this case the copolymers are constituted by alternated blocks of conjugated (chromophor) and non-conjugated (spacer) segments. The emission color control is achieved by the control of the length of the conjugated segment [3,4].

Some of these electroluminescent alternating block copolymers present high photoluminescence efficiency in the solid phase, which was attributed to greater excitonic confinement provided by the block copolymer by virtue of phase segregated morphology [5]. One could expect that this characteristic associated to a wide recombination zone inside the polymer layer of a LED also would improve the electroluminescent efficiency due to reduced electrode quenching of excitons. To achieve the control the charge carrier mobility by molecular design is necessary to understand how the mobility is influenced by several of the copolymer characteristics such as chromophore length, space length and substitution.

The positive charge carrier mobilities observed in a series of electroluminescent alternating block copolymers [6-9] is consistent with the fact that a reduction in the spacer length implies in a reduction in the av-

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erage tunneling distance, making charge transport by hopping more facile. When the spacer is maintained constant, higher mobilities observed in polymers with longer conjugated segments have been tentatively explained as being due to a higher conjugated material to spacer material volume ratio, which then reduces the average tunneling distance [6]. The negative charge carrier mobility has again a non-trivial dependence on the spacer length. It has been observed that for short aliphatic segments (spacers) the energetic disorder expressed through the characteristic energy of the electron trap energy distribution in the polymers is temperature dependent [9]. Depending on temperature and spacer length, the molecular forces responsible for the energetic disorder can not more be accommodated by the spacer, leading to a deeper trap distribution into the gap [9].

In this contribution we investigate the charge transport characteristics of the electroluminescent alternating block copolymer presented in Fig. 1 using metal/polymer/metal devices. We demonstrate that similarly to several other organic materials [10-15] and specially, other electroluminescent alternating block copolymers [6-9], electron and hole transport is space-charge-limited for the polymer layer thickness used. We determine the mobilities of positive and negative charge carriers and investigate the application of this block copolymer as emissive layer in LEDs. The theoretical background as well as the procedure adopted in this work for the mobility calculation is similar to that used in earlier reports [6-9], permitting comparison with other electroluminescent alternating block copolymers.

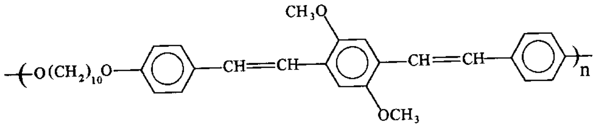


Figure 1. Structure of the electroluminescent alternating block copolymer investigated in this work.

II Space-charge-limited transport

For the case of existence of a single discrete set of shallow traps in solids, at low voltages, electrical conduction is ohmic and the current density is described by [17],

$$j = q\mu_{eff} n_0 \frac{V}{d}, \qquad (1)$$

where q is the electronic charge, μ_{eff} is the effective charge carrier mobility, d is the film thickness, V is the voltage, n_0 is the free carrier density. As the voltage increases, the current is controlled by space-charge. Because of the existence of traps, the current density is expressed as [17] ,

$$J = \frac{9}{8}\epsilon\theta\mu\frac{V^2}{d^3}, \qquad (2)$$

where

$$\theta = \frac{n}{n+n_1} \quad \text{or} \quad \theta = \frac{p}{p+p_1} \qquad (3)$$

for electrons and holes, respectively (n is the density of free electrons, n_t is the density of trapped electrons, p is the density of free holes and p_t is the density of trapped holes). In this case, $\theta\mu \equiv \mu_{eff}$ (μ is the free charge carrier mobility). Taking the temperature dependence of n, p, n_t, p_t and consequently of θ into account, μ_{eff} can be written in the form [9]

$$\mu_{eff} = \mu\frac{N_\nu}{N_t}\exp\left(-\frac{E_t - E_\nu}{\kappa T}\right), \qquad (4)$$

yielding a strong temperature dependence for μ_{eff} and leading to

$$j = \frac{9}{8}\epsilon\mu\frac{N_\nu}{N_t}\exp\left(-\frac{E_t - E_\nu}{\kappa T}\right)\frac{V^2}{d^3}. \qquad (5)$$

In the expressions above N_ν is the density of states in the valence band, N_t is the density of traps, E_f is the relevant Fermi level, E_ν is mobility edge energy for positive charges and E_t is the energy level of the traps; κ is the Boltzmann constant.

To distinguish between μ (which equals μ_{eff} when $\theta \approx 1$) and μ_{eff} a more detailed investigation including temperature dependence of the current [see Eqs. (4) and (5)] must be performed [6,9].

In amorphous materials a single discrete energy level may no longer be a reasonable approximation. In this case, the localized states (traps) density is expected to be in the form of an exponential distribution at energies E within the forbidden energy gap, such that

$$h(E) = \frac{N_t}{E_c}\exp\left(-\frac{E}{E_c}\right), \qquad (6)$$

where E_c is the characteristic energy of the distribution. The $j(V,d)$ dependence in this case is of the form [17]

$$j \propto \frac{V^{m+1}}{d^{2m+1}} \qquad (7)$$

where $m \equiv T_c/T$; $E_c \equiv kT_c$ (T is the absolute temperature and T_c is the characteristic temperature). Thus, if $j(V)$ is measured for different temperatures the $m(T)$ curve can be constructed and the value of E_c can be determined (assuming a temperature independent E_c) using:

$$E_c = kT_c = k\frac{\partial m}{\partial T^{-1}} \qquad (8)$$

In all the cases described above, μ is considered to be independent of the electric field strength though in some cases field dependent mobilities were also reported for several organic compounds (see, for example, Refs. [10-12,18]). As recently demonstrated [19], the experimental $j(V)$ curve cannot be described for the entire range of $j(V)$ data taking the space-charge effects due to low charge carrier mobility into account, neither for the Poole-Frenkel model [20], nor for the charge dipole interaction model [21]. The values obtained using the high field approximation expression due not coincide with that determined with help of Eq.(2) when the high field mobility is extrapolated to $E = 0$ [19]. The values determined in this work using the procedure described in this section, correspond to the field independent mobility case, which is observed at low fields [19].

III Experimental

The metal/polymer/metal devices were prepared on a glass substrate. The bottom metal electrode was evaporated onto the glass and the polymer was spin coated in $CHCl_3$ solution (5 mg/ml) onto this electrode. The top metal electrode was then evaporated onto the polymer layer. The metals used were Al and Au, with work functions (ϕ) of 4.3 eV and 5.1 eV, respectively. The polymer film thickness was measured using a surface profiler. Details concerning sample geometry were as reported earlier [16]. The current-voltage $I(V)$ measurements were made by increasing the voltage from zero to a maximum value at a rate of 0.1 $V.s^{-1}$ and then decreasing to zero at the same rate. Measurements were carried out at room temperature, except when the temperature dependence was determined. The dielectric constant of the polymer was assumed to be 3.

LEDs were constructed in an ITO/copolymer(d = 100 nm)/PMMA:PBD/Alq_3/Al [ITO: indium-tin oxide; PMMA: poly(methyl methacrylate and PBD: 2-(4-biphenylyl)-5-(4-tert-butylphenyl)-1,3,4-oxadiazole; Alq_3: tris(8- quinolinolato) aluminum (d = 8nm)] LED multilayer structure (see Ref. [22] for details). The photoluminescence and the electroluminescent spectra were measured with a SPEX FL-2T2 spectrometer. The luminance was measured with a calibrated ST-900 luminance meter.

IV Results

In Fig. 2 we present the $I(V)$ (I: current; V: applied voltage) characteristics and $I(d)$ (d: copolymer layer thickness) dependence at constant V for an Au/copolymer/Al device, for Au positively biased. In the $I(V)$ curve, three intervals can be distinguished: (a) and (c) corresponding to $j \propto V^2$; and (b) which corresponds to a trap filling region [6,9] where the value of θ, and consequently, μ_{eff} changes abruptly. This $I(V, d)$ dependence corresponds to that expressed by Eq. (2).

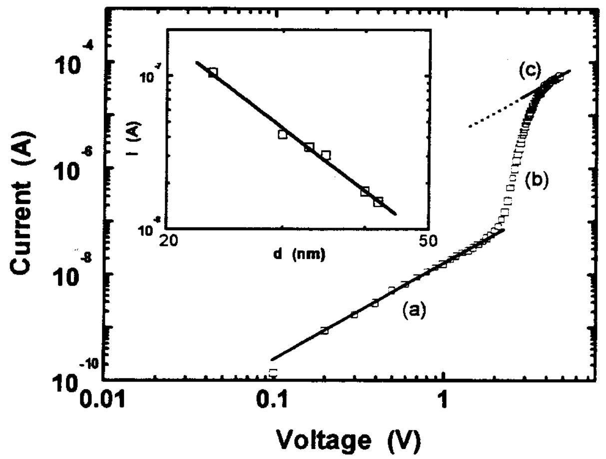


Figure 2. $I(V)$ characteristics of an Au/copolymer/Al device ($d = 40$ nm) for Au positively biased. Inset: $I(d, V = 1\ V)$ dependence for samples with different thickness.

Applying Eq. (2) to the data of segments (a) and (c) of Fig. 2 (15 samples) leads to μ_{eff} equal to $(1.3 \pm 0.3) \times 10^{-10}$ $cm^2/V.s$ and to $(1.4 \pm 0.3) \times 10^{-8}$ $cm^2/V.s$, respectively. The change in the μ_{eff} value confirms that segment (b) corresponds to trap filling. From the inset of Fig. 2 it is possible to observe that, taking the $I(V)$ data from samples with different thickness, for $V = 1V$, $\frac{\partial log I}{\partial log d} \approx -3$, just as also expected from Eq. (2).

In Fig. 3 we present the $I(V)$ characteristics of an Au/copolymer/Al device for different temperatures. The measured range corresponds to segment (a) in Fig. 2. In the inset, we present the temperature dependence of μ_{eff}. Using Eq. (4), 0.4 eV was determined. The $I(V)$ curve is almost temperature independent for voltages larger than the trap filling voltage.

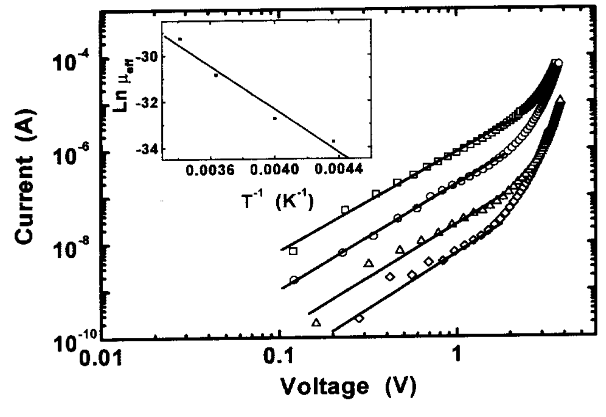


Figure 3. $I(V)$ characteristics of an Au/copolymer/Al device ($d = 30$ nm) at different temperatures (diamonds: 229 K; triangles: 250 K; circles: 275 K; squares:293 K) for Au positively biased. Inset: Temperature dependence of μ_{eff}.

In Fig. 4 we present the $I(V)$ characteristics of an Al/copolymer/Al device. This $I(V)$ curve is characterized by three distinct segments: (a) ohmic, i.e., $j \propto V^{m+1}$; (b) exponential distribution of traps, i.e.,

$j \propto V^{m+1}/d^{2m+1}$ and; (c) $j \propto V^2$. In the inset of Fig. 4, we present the $V(d^2)$, where $V(I = 1 \times 10^{-8}$ A) was taken for different samples (with different d). For $m > 2$, V is expected to be approximately proportional to d^2 [see Eq. (7)] if the transport is space-charge limited due to an exponential distribution of traps. Applying Eq. (2) to the segment (c) of the $I(V)$ curves of 14 samples, we obtained $\mu_{eff} = (5.9 \pm 2.3) \times 10^{-11}$ cm^2/V.s.

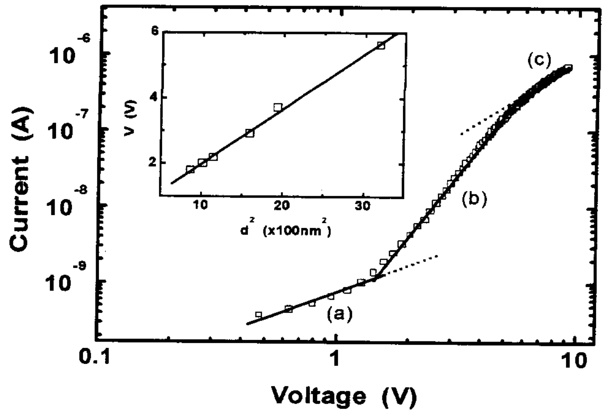


Figure 4. $I(V)$ characteristics of an Al/copolymer/Al device ($d = 44$ nm). Inset: $V(d^2, I = 1 \times 10^{-8}$ A) dependence for samples with different thickness.

In Fig. 5, $I(V)$ curves taken at different temperatures using Al/copolymer/Al devices are presented (the voltage range was limited to avoid possible device degradation). The values $m(T)$ were determined and $E_C \simeq 0.12$ eV calculated using Eq. (8). The $m(T)$ data are presented in the inset of Fig. 5.

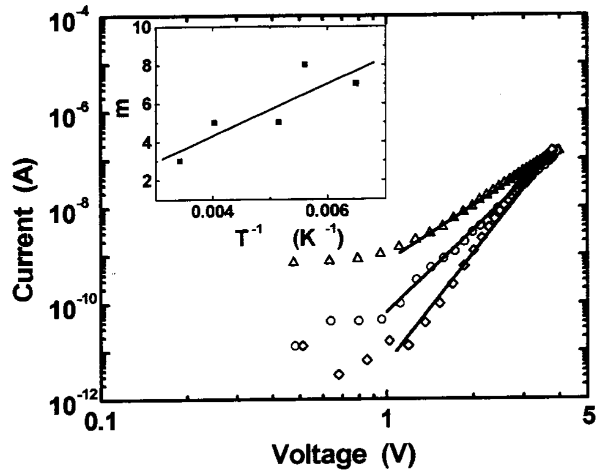


Figure 5. $I(V)$ characteristics of an Al/copolymer/Al device (d = 40 nm) at different temperatures (diamonds: 154 K; circles: 194 K; triangles:292 K). Inset: m as a function of T^{-1}.

In Fig. 6 the photoluminescence (PL) spectrum of the copolymer is compared with the electroluminescence (EL) spectrum of an ITO/copolymer/PMMA:PBD/Alq3/Al LED. In Fig. 7 we compare the current and the brightness evolution with increased applied voltage for the ITO/copolymer/PMMA:PBD/Alq3/Al LED.

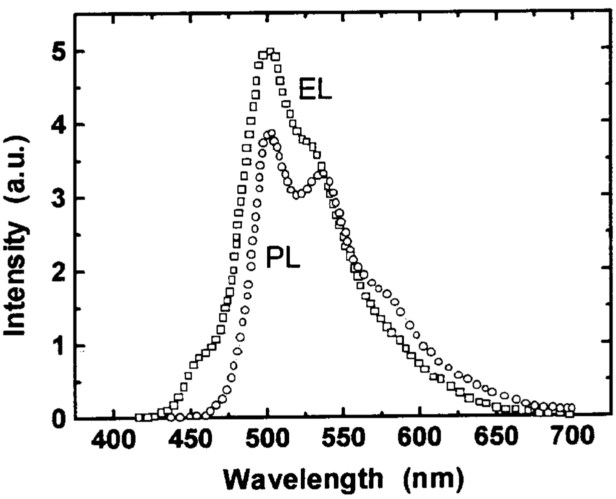


Figure 6. Photoluminescence spectrum of the copolymer is compared with the electroluminescence spectrum of an ITO/copolymer/PMMA:PBD/Alq$_3$/Al LED.

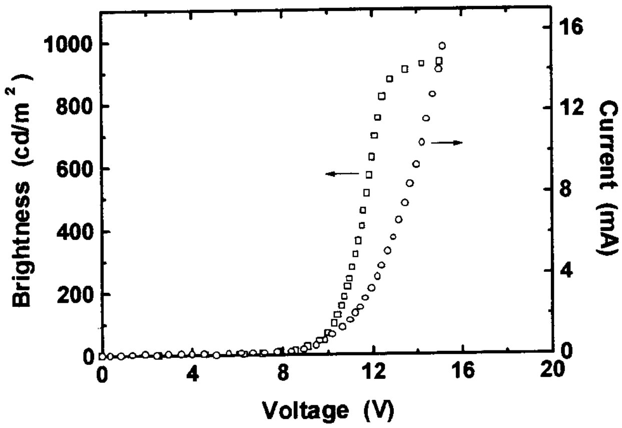


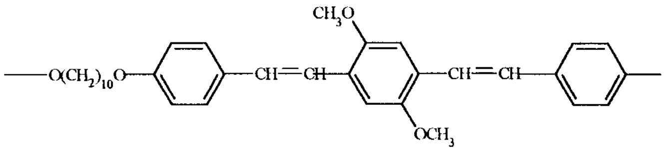
Figure 7. Comparison of the current and the brightness evolution with increased applied voltage for the ITO/copolymer/PMMA:PBD/Alq$_3$/Al LED.

V Discussion

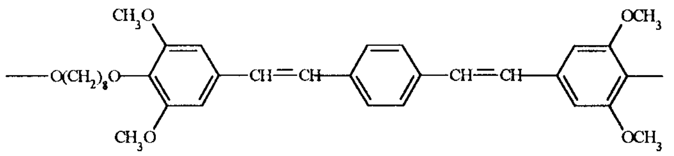
The $I(V)$ curve presented in Fig. 2 is obtained using an Au/copolymer/Al device. Considering the work functions of the electrodes and the fact that the values of ionization potential of the chromophores are expected to be near to those observed in PPV oligomers, the charge transport is predominantly due to positive charge carriers. The μ_{eff} values determined using these devices are, for these reasons, those of positive charge carriers. Considering that the mobility is temperature dependent before trap filling [segment (a) in Fig. 2] and almost temperature independent for larger voltages, the μ value determined from segment (c) corresponds to the free positive charge carrier ($\theta \approx 1$).

The current in Fig. 5 also arrives a region [segment (c) of Fig. 4] where it becomes temperature independent. Consequently, the charge carrier mobility extracted from this segment is temperature independent, indicating that all trap levels are full ($\theta \approx 1$). Considering that this mobility value is lower than those observed in Au/copolymer/Al devices, it is attributed to another type of charge carrier, i.e., to negative charge carriers.

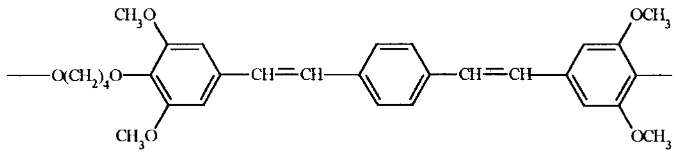
In Fig. 8 we compare the reported charge carrier mobilities for different electroluminescent block copolymers [6,8,9]. In the series of polymers the conjugated segments are of the same length, with spacers of decreasing length. As shown in Fig. 8, both, the negative charge carrier mobility and the positive charge carrier mobility increase with decreasing spacer length.



Copolymer - I	
μ_e [cm^2/Vs]	6×10^{-11}
μ_h [cm^2/Vs]	1×10^{-8}



Copolymer - II	
μ_e [cm^2/Vs]	5×10^{-10}
μ_h [cm^2/Vs]	4×10^{-7}



Copolymer - III	
μ_e [cm^2/Vs]	8×10^{-10}
μ_h [cm^2/Vs]	2×10^{-6}

Figure 8. Comparison of the positive (μ_h) and negative (μ_e) charge carrier mobilities for different block copolymers recently investigated.

The characteristic energy of the electron trap distribution of copolymer I (0.12 eV) is significantly higher than observed in copolymers II and III [0.06 eV and 0.05 eV (at room temperature), respectively]. Polymer I has the longest spacer, so that it should be expected that it would be able to accommodate tensions and reduce the energetic disorder, contrarily than experimentally observed. This disagreement may suggest that the methoxy groups present in the central ring of the chromophore in this copolymer are responsible for the increase in the energetic disorder.

It has been observed that poly(2-methoxy-*p*-phenylene vinylene), MeO-PPV, presents a lower degree of structural order than PPV and poly(2,5-dimethoxy-*p*- phenylene vinylene), DMeO-PPV [26]. This fact was attributed to the copolymer structure exhibited by MeO-PPV due to asymmetric ring substitution. This observation may be partially applied to copolymer I. Even for a planar chromophore, two different configurations of the chromophore are possible due to rotation of the central ring, leading to different possible interactions between neighboring molecular segments, increasing energetic disorder.

Copolymer I is green-emitting (see Fig. 6) indicating that the methoxy bi- substitution in the central ring of the chromophore produces a red-shift in the electroluminescent spectrum. Copolymers II and III are blue-emitting and the non- substituted analogue of copolymer I has an emission maximum near 470 nm [23]. It has been observed that both, the absorption and the emission spectra of electroluminescent alternating block copolymers are determined by their chromophoric units, without influence of the spacer length [24]. It is also observed that copolymer I and another copolymer with shorter spacer, but with the same chromophoric unit [25], have similar emission spectra, which confirms that the red- shift is due to the introduced methoxy groups.

LEDs constructed with an analogue copolymer with shorter spacer have presented higher EL intensity as well as lower threshold voltage for light emission [25]. This may be attributed in part to the higher mobility expected for the copolymer with shorter spacer, indicating that from the charge transport point of view copolymers with shorter spacers (but long enough to permit accommodation of forces that would promote energetic disorder) are most appropriate for LED applications.

VI Conclusion

We investigate the transport characteristics of an electroluminescent alternating block copolymer with a methoxy bi-substituted chromophore and determine the mobility of positive and negative charge carriers in this polymer.

We observed that the methoxy substitution produces, when this polymer is compared with analogues with the same conjugated segment length, a red-shift in the emission spectra. The charge carrier mobilities in this polymer are lower than that observed in other block copolymers with conjugated segments of the same length, but with shorter spacers.

LEDs constructed using this block copolymer as emissive material present a brightness of ~ 900 cd/m^2 when operating at 12.5 V.

Acknowledgements

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