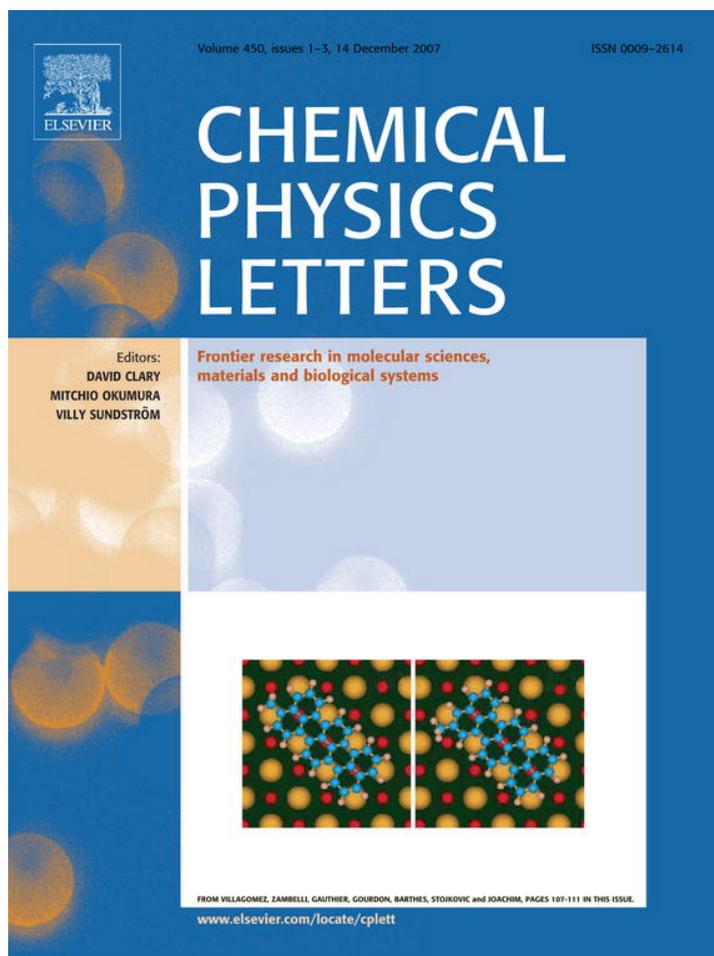


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Solvent mediated enhanced mobility of PPV films cast under the presence of a static electric field

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Abstract

Application of a high voltage static electric field during casting increases charge carrier mobility and reduces nanostructure within MEH-PPV thin films. Greater enhancement occurs in films formed from a high static dipole moment solvent (chlorobenzene) than from one having a low moment (toluene). Analysis by Bassler's Gaussian Disorder Model indicates that the electric field decreases positional disorder – the effect being greater for the higher static dipole moment solvent. This suggests that the interaction of the electric field with MEH-PPV during deposition is indirect rather than direct, being mediated by the evaporating solvent.

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1. Introduction

Luminescent conjugated polymer based optical devices such as light emitting diodes are interesting both from a theoretical and practical point of view since a wide range of their properties, such as solubility and color of light emission, can be tuned via chemical synthesis allowing the engineering of molecules to meet specific requirements. In addition, polymer coatings can be easily applied over large areas and on a variety of substrates raising the potential of low cost fabrication. However, low charge mobility, compared to crystalline silicon severely limits the range of applications [1].

Considerable effort has been expended on efforts to increase charge mobility both through chemical synthesis and the application of processing techniques such as annealing and solvent modification. Recently a number of groups have applied a static high voltage electric field

during the casting of MEH-PPV thin films and observed an enhancement of charge mobility ranging from a factor of two [2] to a factor of ten [3,4]. Enhancement has been reported for a variety of solvents and for both spin [5] and drop-cast [2] films.

The morphological basis for this enhanced mobility has been investigated using the techniques of wide-angle and small-angle X-ray scattering (WAXS and SAXS, respectively). In regular drop-cast films, preferentially uniaxial-oriented nano-domains are embedded in a disordered (amorphous) matrix. Such nano-domains compose ~50% of the film volume [6]. In a similar study of films dropped in the presence of an electric field, the scattering peaks characteristic of these nano-domains were absent, suggesting that the application of the electric field had resulted in a largely amorphous structure without grain boundaries [3]. The conclusion was that elimination of grain boundaries results allows for an increase in charge mobility [4].

While the above papers have addressed the link between morphology and charge transport, the mechanism for this reduction in nano-domains has not been adequately addressed. It seems unlikely that a direct interaction

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between a static electric field and the nominally centrosymmetric and nonpolar ground state PPV molecules [7] is responsible for this morphological change. An alternative explanation is a solvent mediated interaction i.e., the static electric field interacts with the solvent and the solvent then interacts with the polymer.

The goal of this Letter is to show that interaction of electric field is not with the polymer directly but with the solvent which then interacts with the polymer. In order to do this MEH-PPV thin films were prepared under identical conditions with only the solvent changed. The first set of films was prepared using a solvent characterized by a high dipole moment, while the second was prepared using a solvent characterized by a low dipole moment. In the first case, solvent molecules are expected to align with the electric field while in the second case no interaction is expected. If the morphological changes are a solvent mediated effect then one expects that for the case of the low dipole moment solvent, the presence or absence of an electric field is not significant, while for the high dipole moment, the presence or absence of the electric field will lead to significant differences in mobility.

2. Experimental

Thin films of $\sim 3.5 \mu\text{m}$ thickness were prepared by drop-casting method from 5 mg/cc of MEH-PPV on pre-cleaned ITO-coated substrates. The solvent was allowed to vaporize slowly in a solvent-rich atmosphere to get good optical quality films. During the drop-casting process, films were produced with ('e-drop-cast') and without ('drop-cast') an 3.5 kV electric field being applied perpendicular to the substrate [3,4]. The films were then dried for 24 h at room temperature and the residual solvent removed by placing in a high vacuum chamber. Subsequently 1000 Å thick aluminum electrodes were thermally evaporated by the shadow mask procedure to yield the active area of 4 mm² for time of flight (TOF) studies. The resulting device capacitance was ~ 30 pF giving CV ~ 1200 pC at the 40 V used in experiments. The samples were then transferred to a temperature-controlled vacuum cryostat, and kept in the vacuum ($\sim 10^{-6}$ mbar) for 12 h prior to the measurements. Charge carriers were generated at the ITO/polymer interface by 5 ns pulses from a frequency doubled YAG laser ($\lambda = 532$ nm, 50 mW). In order to ensure that the electric field was not perturbed, the injected charge was kept below ~ 100 pC. The intersection of asymptotes to the plateau and the declining slope of the current transient was used to determine the transit times (t_{tr}) and hence mobility (μ) from

$$\mu = \frac{L^2}{Vt_{\text{tr}}}$$

where V is the applied voltage and L is the thickness of the film. Temperature dependent mobility was measured at temperatures ranging from 225 to 325 K. The signal to noise ratio was increased by averaging over 1000 pulses.

The resulting signal to noise ratio and the time resolution of the TOF set up determined the lowest and highest temperature in this investigation, respectively [8]. Both the 'drop-cast' and 'e-drop-cast' films were prepared from the same solution batch.

The above experiment using the same pristine MEH-PPV, was completed for two solvents, one having a low static dipole moment (0.36 D, toluene) and the other a large static dipole moment (1.6 D, chlorobenzene). These solvents were chosen due to their vastly different dipole moments, similar structure and the fact that optically homogeneous films having identical optical spectra (i.e., PL and absorption) can be formed from both solvents [9]. (Identical optical spectra implies the degree of inter-chain interaction, an important factor in determining charge transport [10], is the same for films formed from both solvents. The use of the same MEH-PPV for all samples ensures that defect and hole trap state density, also important in charge transport, are the same for all films [11]).

Results were analyzed using the commonly applied Gaussian Disorder Model of Bässler and coworkers [12], namely:

$$\mu(E, T, \hat{\sigma}, \Sigma) = \mu_0 \exp\left(-\frac{2}{3}\hat{\sigma}\right) \exp\left(C\sqrt{E}(\hat{\sigma}^2 - \Omega)\right)$$

where E is the applied electric field, T is the absolute temperature (K), $\hat{\sigma}$ is the normalized energy disorder ($\sigma/k_{\text{B}}T$), Σ is the positional disorder, μ_0 is the mobility at infinite absolute temperature and zero field, and C is an empirical constant. Ω is defined as follows: if $\Sigma > 1.5$, $\Omega = \Sigma^2$ otherwise $\Omega = 2.25$. k_{B} is the Boltzmann constant. The energy disorder parameters (σ) were obtained by plotting $\ln(\mu(E=0))$ against $1/T^2$. The position disorder parameters (Σ) were obtained by plotting the slope of the field dependent mobility against $\hat{\sigma}^2$ for each of the films.

3. Results and discussion

Figs. 1 and 2 compare the measured field dependent mobility for films drop-cast in the presence and absence of a static electric field for the low dipole moment and large dipole moment solvents, respectively. (A typical TOF transient pulse is shown in supplementary Fig. S1) For both solvents, application of the static electric field during the casting process leads to increased charge mobility. However, the increase is much more pronounced in the case of the chlorobenzene than for toluene. This is seen clearly Fig. 3 where the enhancement of mobility for the two solvents as a function of electric field is compared. The enhancement is greatest for low electric fields and decreases monotonically as the electric field is increased. In the case of the low dipole moment solvent, the enhancement in field dependent mobility approaches one at high electric field. Across the complete range of applied electric fields, films cast from the large dipole solvent exhibit significantly higher charge mobility.

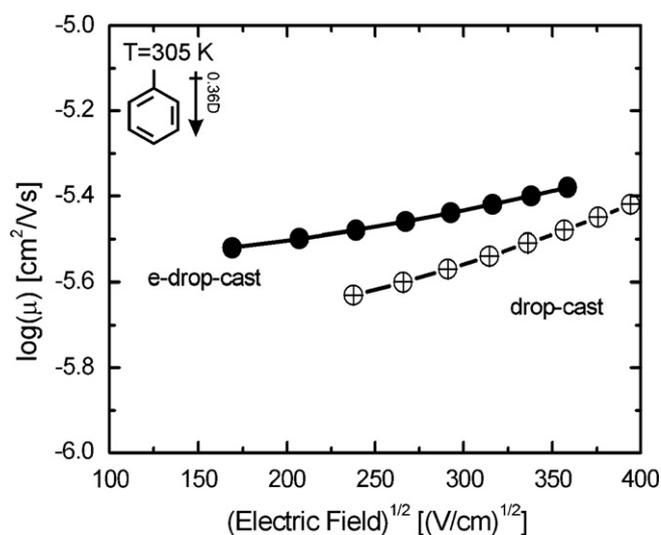


Fig. 1. Comparison of field dependent mobility for films formed with toluene as the solvent drop-cast in the presence and absence of a static electric field.

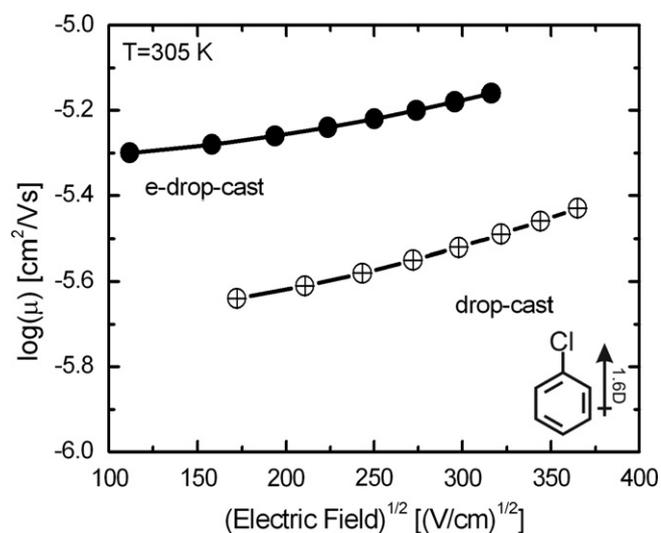


Fig. 2. Comparison of field dependent mobility for films formed with chlorobenzene as the solvent drop-cast in the presence and absence of a static electric field.

To gain further insight into the origin of these differences, mobility was measured as a function of electric field and temperature in order to derive the positional and energy disorder parameters for the two films [12,13]. The results for the 4 films are tabulated in Table 1. As seen in the table energy disorder (σ) is ~ 60 meV in all cases. It is only slightly affected by either solvent choice or application of electric field. The application of the electric field increases this only slightly. Significant differences, however, are seen behaviour of the positional disorder parameter for the four films. While the positional disorder parameter is similar for the two drop-cast films, the application of the static electric field results in a decrease in positional disorder (i.e., increase in positional order) for both films. This

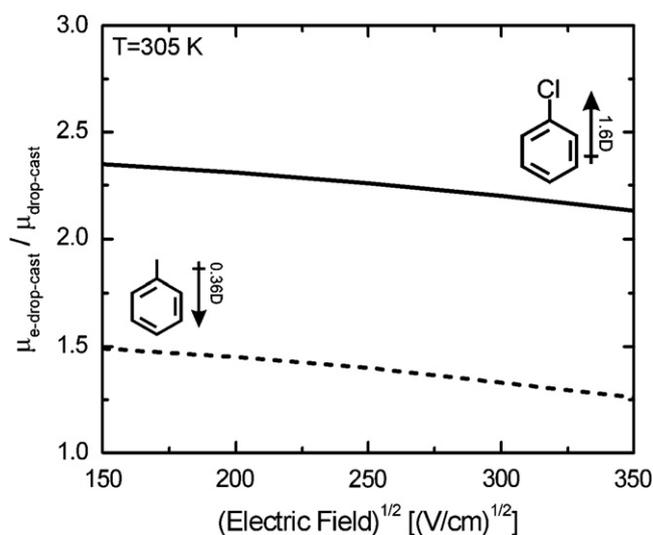


Fig. 3. Comparison of the mobility enhancement at as a result of an applied static electric field for films formed with toluene and chlorobenzene as the solvent.

Table 1

Comparison of energy and positional disorder for films formed from toluene and chlorobenzene as the solvent with and without the presence of a static electric field

Solvent	E-field [ON OFF]	GDM disorder parameters	
		Energy (σ , meV)	Positional (Σ)
Toluene	OFF	57	4.2
Toluene	ON	61	3.2
Chlorobenzene	OFF	60	4.4
Chlorobenzene	ON	63	1.6

change is greater in the case of the film cast from MEH-PPV dissolved in the chlorobenzene than for that dissolved in toluene. In contrast to the film formed from the low dipole moment solvent where positional disorder within the film is still substantial, the positional disorder is $\ll 2.25$ in the film formed from the high dipole moment solvent. This indicates that in the latter film, variation in the effective distances between hopping sites has been effectively eliminated. Structure within the film has been decreased.

The above results clearly indicate that the interaction of the electric field with the forming MEH-PPV thin film is a solvent mediated effect. While mobility is increased for both films, the effect is much efficient in the case of the high dipole moment solvent (chlorobenzene) than for the low dipole moment solvent (toluene). While positional disorder is reduced and mobility is increased for both solvents, the effect is much efficient in the case of the high dipole moment solvent than for the low dipole moment solvent.

Two possible explanations exist for this decrease in positional disorder (i.e., increase in global homogeneity) either a reduction of nano-domains or improved 'long range' alignment. The small and wide-angle X-ray diffraction

studies of Jeng et al. [6,3] tend to favour the former explanation. In their investigation of films formed with chlorobenzene as a solvent, they demonstrated that drop-cast films of MEH-PPV are composed of two phases, namely, ordered nano-domains embedded in an amorphous polymer matrix. Application of a static electric field during casting was found to inhibit (but not eliminate) the formation of the nano-domain phase. As this correlates well with the decrease in positional disorder obtained in the Bässler model, it seems likely that decreases in positional disorder reflect the reduction of nano-domains. The much smaller decrease in the positional disorder parameter seen in the films cast from the low dipole moment solvent indicates that the strength of interaction between the electric field and the solvent dipole moment was insufficient to orient the solvent molecules and thus significantly disrupt the formation of ordered nano-domains.

Finally it is appropriate to address the question about the strength of applied electric field necessary to orientate the solvent molecules in light of random thermal motion. Roughly speaking at room temperature the thermal motion energy of a solvent molecule is on the order of 10^{-21} J. This compares to an average interaction energy ($H = \mathbf{p} \cdot \mathbf{E}$) of the solvent's dipole (\mathbf{p}) with the electric field (\mathbf{E}) on the order of 10^{-22} J for an applied potential of 3.5 kV and electrode separation of ~ 5 mm. The similar order of magnitude of these two energies indicates that firstly the choice of solvent will strongly influence the degree of solvent alignment and secondly, that the alignment of the solvent molecules is not complete (i.e., at higher electric fields it might be possible to further increase the film homogeneity).

4. Conclusions

In conclusion, films drop-cast in the presence of a static electric field formed from MEH-PPV dissolved in chlorobenzene (large dipole moment) exhibit much greater enhancement in mobility (relative to those drop-cast without an electric field being present) compared to films formed using toluene (low dipole moment) as solvent. Analysis of experimental results using the Bässler GDM model indicate that this correlated with a substantial decrease in positional disorder for the former film. The

above data strongly suggests that the static electric field interacts indirectly with the forming MEH-PPV film via the slowly evaporating solvent. While in the case of chlorobenzene, its high dipole moment allows the static electric field to cause significant alignment of the solvent molecules, the effect is much more limited in the case of low dipole moment solvent toluene. The alignment of the solvent molecules and resulting internal electric fields, thus serve to inhibit domain formation.

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Appendix A. Supplementary data

Supplementary data associated with this article can be found, in the online version, at [doi:10.1016/j.cplett.2007.09.089](https://doi.org/10.1016/j.cplett.2007.09.089).

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