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Published in:
Journal of Applied Physics

DOI:
10.1063/1.1928314

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Document Version
Publisher's PDF, also known as Version of record

Publication date:
2005

Link to publication in University of Groningen/UMCG research database

Citation for published version (APA):

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Optimization of the charge transport in poly(phenylene vinylene) derivatives by processing and chemical modification

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(Received 25 October 2004; accepted 13 April 2005; published online 20 June 2005)

We present a systematic study of the influence of the processing conditions on the charge-carrier mobility in hole-only diodes and field-effect transistors (FETs) based on alkoxy-substituted poly(p-phenylene vinylene) (PPV). It is demonstrated that by chemical modification from asymmetrically to fully symmetrically substituted PPVs the mobility in both types of devices can be significantly improved. Furthermore, for symmetrical PPVs the mobility is strongly dependent on processing conditions, such as choice of solvents and annealing conditions. The increase in mobility is accompanied by a strong enhancement of the anisotropy in the charge transport. Ultimately, mobility of up to $10^{-2}$ $\text{cm}^2/\text{Vs}$ in FETs and $10^{-5}$ $\text{cm}^2/\text{Vs}$ in hole-only diodes have been achieved.


I. INTRODUCTION

Solution-processable conjugated polymers have an important potential use in optoelectronic devices such as light-emitting diodes (LEDs),\textsuperscript{4,5} field-effect transistors (FETs) and integrated circuits,\textsuperscript{4,6} and solar cells.\textsuperscript{7} In order to improve the device performance research efforts have been focused on developing polymers such as poly(p-phenylene vinylene) (PPV) for LEDs and polythiophene for FETs. Besides, the device performance is controlled by the film morphology, which can be manipulated by processing factors such as various organic solvents, solution concentrations and temperatures, spin-coating procedures, and annealing temperatures.\textsuperscript{5}

It has been demonstrated that thermal treatment of the disordered polymers can modify the film morphology and thus improve the electrical properties of the LEDs such as quantum efficiency, turn-on voltage, and electroluminescence.\textsuperscript{8,9} It has been suggested that when annealing, e.g., poly(2-methoxy-5-(2’-ethyl-hexyloxy)-1,4-phenylene vinylene) (MEH-PPV) at a temperature higher than glass transition temperature ($T_g$), the polymer chains relax. As a result, a smoother interface contact between the polymer and the cathode is formed, resulting in an increased electron injection. Other studies focused on the influence of the solvent on the polymeric film properties.\textsuperscript{9,12} It has been shown that the absorbance and the photoluminescence (PL) spectrum of the MEH-PPV film obtained from chlorobenzene solution, which is an aromatic solvent, are redshifted compared with those in tetrahydrofuran, which is a nonaromatic solvent. This shift was attributed to the formation of aggregates, which is solvent dependent. NMR studies of the polymer solution (MEH-PPV in toluene) revealed well-packed chains formed in order to minimize polymer–solvent interactions. The increase of the field-effect mobility from toluene to chlorobenzene solution in poly(2-methoxy-5-(3′, 7′-dimethyloctyloxy)-p-phenylene vinylene) (OC$_1$OC$_{10}$-PPV) (polymer A from Table I) FET has also been explained on the basis of a modification of the polymer morphology.\textsuperscript{13}

This work is focused on mobility measurements in hole-only diodes and FETs of alkoxy-substituted PPVs. The results are related to a change in the polymer morphology determined by different side chains, organic solvents, and annealing temperature.

II. EXPERIMENT

The general chemical formula of the alkoxy-substituted PPVs used as active layers in field-effect transistors and hole-only diodes is presented in Fig. 1. These polymers consist of symmetric and/or asymmetric monomers depending on the substitution pattern of the phenyl ring $R^1$, $R^2$, and $R^3$ (see Table I). Polymerization followed a modified Gilch dehydrohalogenation procedure,\textsuperscript{14,15} and it is explained in more detail in Ref. 16. Polymer poly[2-(4-(3′,7′-dimethyloctyloxy phenyl))-co-2-methoxy-5-(3′,7′-dimethyloctyloxy)-1,4-phenylene vinylene] (NRS-PPV) has been synthesized according to the procedure indicated in Ref. 17. Molecular weights have been determined by gel permeation chromatography (GPC) and they are in the range of 1.3 $\times$ 10$^5$–1.4 $\times$ 10$^6$ g/mol. The polymers are characterized in field-effect transistors and hole-only diodes. The field-effect transistor has been made using a highly doped $n^+$-Si as gate electrode and a 200-nm thermally grown SiO$_2$ thin film used as gatedielectric. Using conventional photolithography, gold source and drain elec-

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In both field-effect and hole-only devices. In Table I the val-
ues of the hole mobility in the two types of devices are
presented. For a direct comparison we first used for all the
polymers only one solvent, namely, chlorobenzene.

The field-effect mobility has been determined from the
transfer characteristics of the FETs in the linear operating
regime at a gate voltage \( V_g = -19 \) V and a drain voltage \( V_d = -2 \) V. Figure 2 presents the transfer characteristics for
FETs of polymers A and J spin coated from a chlorobenzene
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10\(^{-4}\)–6 \(\times 10^{-6}\) cm\(^2\)/Vs, while for the
asymmetric/symmetric (class 2) and symmetric PPVs (class
3) it is in the range of 7 \(\times 10^{-4}\)–6 \(\times 10^{-3}\) cm\(^2\)/Vs. The in-
crease of the source-drain current between asymmetric and
symmetric PPVs (see Fig. 2) is quantitatively in agreement
with the enhancement of the mobility.

The current in PPV-based hole-only diodes has been shown
to depend quadratically on the voltage and exhibit a
third-power dependence on sample thickness.\(^{18}\) This behavior is characteristic of a space-charge limited current
(SCLC). The occurrence of SCLC enables us to directly de-
terminate the hole mobility from the current density–voltage
\((J–V)\) characteristics. It should be noted also that a material
with shallow traps would exhibit an identical voltage and

<table>
<thead>
<tr>
<th>Polymer ((n, m))</th>
<th>(R^1)</th>
<th>(R^2)</th>
<th>(R^3)</th>
<th>(\mu_{\text{FET}}) ((\text{cm}^2/\text{Vs}))</th>
<th>(\mu_{\text{LED}}) ((\text{cm}^2/\text{Vs}))</th>
</tr>
</thead>
<tbody>
<tr>
<td>Class 1 NRS</td>
<td>C</td>
<td>C</td>
<td>C</td>
<td>1 (\times 10^{-4})</td>
<td>1 (\times 10^{-8})</td>
</tr>
<tr>
<td>Asymmetric A (1,0)</td>
<td>CH3</td>
<td>C(<em>{10})H(</em>{21})</td>
<td>4 (\times 10^{-4})</td>
<td>5 (\times 10^{-7})</td>
<td></td>
</tr>
<tr>
<td>PPVs B (1,0)</td>
<td>CH3</td>
<td>C(<em>{8})H(</em>{17})</td>
<td>5 (\times 10^{-4})</td>
<td>5 (\times 10^{-7})</td>
<td></td>
</tr>
<tr>
<td>Class2 C (0.5,0.5)</td>
<td>CH3</td>
<td>C(<em>{10})H(</em>{21})</td>
<td>C(<em>{10})H(</em>{21})</td>
<td>1 (\times 10^{-3})</td>
<td>6 (\times 10^{-6})</td>
</tr>
<tr>
<td>Asymmetric D (0.06,0.94)</td>
<td>CH3</td>
<td>C(<em>{8})H(</em>{17})</td>
<td>C(<em>{10})H(</em>{21})</td>
<td>1 (\times 10^{-3})</td>
<td>2 (\times 10^{-6})</td>
</tr>
<tr>
<td>symmetric PPVs E (0.5,0.5)</td>
<td>CH3</td>
<td>C(<em>{10})H(</em>{17})</td>
<td>C(<em>{10})H(</em>{17})</td>
<td>7 (\times 10^{-4})</td>
<td>3 (\times 10^{-6})</td>
</tr>
<tr>
<td>Class 3 F (0,1)</td>
<td>CH3</td>
<td>C(<em>{10})H(</em>{17})</td>
<td>9 (\times 10^{-4})</td>
<td>4 (\times 10^{-6})</td>
<td></td>
</tr>
<tr>
<td>Symmetric PPVs G (0.5,0.5)</td>
<td>C(<em>{8})H(</em>{17})</td>
<td>C(<em>{8})H(</em>{17})</td>
<td>C(<em>{14})H(</em>{17})</td>
<td>6 (\times 10^{-3})</td>
<td>5 (\times 10^{-6})</td>
</tr>
<tr>
<td>H (0.5,0.5)</td>
<td>C(<em>{10})H(</em>{21})</td>
<td>C(<em>{10})H(</em>{21})</td>
<td>C(<em>{14})H(</em>{21})</td>
<td>2 (\times 10^{-3})</td>
<td>6 (\times 10^{-6})</td>
</tr>
<tr>
<td>I (0.5,0.5)</td>
<td>C(<em>{3})H(</em>{23})</td>
<td>C(<em>{11})H(</em>{23})</td>
<td>C(<em>{14})H(</em>{23})</td>
<td>2 (\times 10^{-3})</td>
<td>9 (\times 10^{-6})</td>
</tr>
<tr>
<td>J (0.5,0.5)</td>
<td>C(<em>{12})H(</em>{25})</td>
<td>C(<em>{12})H(</em>{25})</td>
<td>C(<em>{14})H(</em>{25})</td>
<td>2 (\times 10^{-3})</td>
<td>2 (\times 10^{-6})</td>
</tr>
</tbody>
</table>

**FIG. 1.** Chemical structure of alkoxy-substituted PPVs (a) and NRS-PPV (b).

**FIG. 2.** Transfer characteristics of polymer A and polymer J FETs \((W = 20 \text{ mm}; L = 10 \mu \text{m})\). Both polymers were spin coated from chlorobenzene.

Trodes were defined onto the insulator with channel width
\(W = 2.5–20 \) mm and length \(L = 10–40 \mu \text{m}\). The transistor is
finished by spin-coating the alkoxy-substituted PPV layer
from different solvents. The transfer characteristics have
been measured in the linear operating regime of the transistor
using a Keithley Semiconductor Characterization System
4200. The hole-only diode consists of a single polymer layer
sandwiched between a prepatterned indium tin oxide (ITO)
electrode used as hole injector and a thermally evaporated
gold electrode on top of the polymer in order to block the
electrons. The polymer layer has a thickness \(h\) in the range of
60–300 nm and was spin-coated from toluene or chloroben-
zeine in a \(\text{N}_2\) atmosphere. The electrical measurements for the
hole-only diode were performed with a Keithley 2400
Sourcemeter in a \(\text{N}_2\) atmosphere.

**III. RESULTS AND DISCUSSION**

**A. Chemical structure**

In order to analyze the influence of the substitution pat-
tern (asymmetrical or symmetrical) of solution-processable
alkoxy-substituted PPVs on the charge-carrier mobility, we
measure the electrical transport properties of these polymers
in both field-effect and hole-only devices. In Table I the val-
ues of the hole mobility in the two types of devices are
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polymers only one solvent, namely, chlorobenzene.

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terminate the hole mobility from the current density–voltage
\((J–V)\) characteristics. It should be noted also that a material
with shallow traps would exhibit an identical voltage and
thickness dependence, and the observed mobility would be an effective mobility in that case, including trapping effects. However, transient measurements demonstrated that the measured mobility does not include trapping effects.\(^{19}\) In Fig. 3 the \(J-V\) characteristics of polymers C and I are presented, from which it can be observed that the current depends quadratically on the voltage. We show that the mobility increases from class 1 to class 3, namely, from \(1 \times 10^{-8} - 5 \times 10^{-7}\) cm\(^2\)/V s to \(2 \times 10^{-6} - 9 \times 10^{-6}\) cm\(^2\)/Vs. In a PPV-based diode \(9 \times 10^{-6}\) cm\(^2\)/Vs is the highest mobility value reported so far. The hole mobility determined for the symmetric PPVs is more than three times higher than for the asymmetric ones, while the field-effect mobility is at least a decade higher. This can be explained by the fact that the chemical modification of PPV influences both the electronic\(^{20,21}\) and the morphologic properties in terms of interchain distance, orientation, and packing of the polymer chains. Using the technique of phase-imaging scanning force microscopy\(^{22}\) it has been demonstrated that the symmetrical PPVs exhibit an increased regularity and a better ordering in the solid state. This results in a reduced energetic disorder, better interchain interaction, and, as a consequence, a better charge transport.

B. Annealing

There is evidence in the literature that thermal treatment improves the transport properties in LEDs.\(^{8}\) Here, we focus on the influence of annealing on field-effect transport properties. The PPV FETs were thermally treated in a temperature range of 80–200 °C for 5–120 min. For the asymmetric PPVs (class 1) little improvement of the mobility has been observed after annealing. All the other substituted PPVs (classes 2 and 3) showed an increase in the mobility for annealing temperatures lower than 110 °C. A typical example of such an annealing experiment is presented in Fig. 4 for polymer J. As it can be seen from Fig. 4, the field-effect mobility increased from \(2 \times 10^{-3}\) cm\(^2\)/Vs after spin coating to \(7 \times 10^{-3}\) cm\(^2\)/Vs after annealing the FET at 110 °C. An even higher increase has been observed for polymer I, for which the field-effect mobility increased from \(2 \times 10^{-3}\) cm\(^2\)/Vs after spin coating to \(1 \times 10^{-2}\) cm\(^2\)/Vs after annealing at 110 °C. This value is the highest reported for a solution-processable PPV in a FET.

C. Solvent

Electronic properties of conjugated polymer films are also affected by the organic solvents from which the polymer is spin coated. In the case of different solvents, different film morphologies may occur depending on the nature of the solvent and the solubility of the polymer. By using different solvents in hole-only diodes made from asymmetric PPVs we do not observe any difference in hole mobility. Figure 5 shows the electrical characteristics of the hole-only diode using as active layer the symmetric polymer F spin coated from toluene and chlorobenzene. The experimental zero-field mobility determined from these measurements is \(4 \times 10^{-6}\) cm\(^2\)/Vs for the chlorobenzene solution and \(1 \times 10^{-5}\) cm\(^2\)/Vs for the toluene solution. Thus, the zero-field mobility in hole-only devices of the symmetrical polymer F varies with a factor of two in the case of two aromatic solvents. We observed this trend for other symmetric PPVs as well. Differences in mobility in the LED configuration have also been observed for PPV films spin coated from aromatic (chlorobenzene) and nonaromatic (tetrahydrofuran) solvents.\(^{9,10}\)
In Fig. 6 the effect of the solvent on the field-effect mobility and the UV absorption is presented for polymer E. The field-effect mobility shows a strong increase for the films spin coated from aromatic solvents in comparison with those obtained from nonaromatic solvents, while the absorbance is redshifted for the film obtained from aromatic solvents with respect to that spin coated from nonaromatic solvents. This behavior can be attributed to an increased interchain interaction in polymer films spin coated from solvents such as chlorobenzene as compared to those spin coated from tetrahydrofuran and is reflected in both the mobility and the UV spectra. If we look at the boiling point of the solvents used in this study we can conclude that solvents with low boiling point such as chloroform, CH₂Cl₂, tetrahydrofuran give a very low mobility, while the high boiling-point solvents such as chlorobenzene or xylene give a very high mobility. This can be attributed to the fact that the chains of the polymer spin coated from solvents like chloroform do not have time to rearrange in the polymer network as it happens, for example, for xylene. However, as stated above, we do not observe the same trend in the hole-only diode.

D. Discussion

We have observed that the effects of annealing and solvent on the mobility are very weak for the heavily disordered asymmetric PPVs (class 1). For classes 2 and 3 these effects are relatively large for the field-effect geometry, but small for the hole-only diodes. The explanation is related to the way in which the polymer arranges itself in the film network and also to the way in which the transport takes place in the two electronic devices. In hole-only diodes the transport takes place between the two electric contacts perpendicular to the polymer film, while in field-effect transistors the transport takes place in the plane of the polymer film. A possible anisotropy in the charge transport can be investigated by comparing the transport in hole-only diodes and FETs made from the same semiconductor. From Table I we observe that the field-effect mobility is much higher than the hole-only mobility at high bias at room temperature is entirely due to the carrier-density dependence of the hole mobility.

The procedure for numerically calculating the carrier-density distribution in a FET is represented in Ref. 20. The mobility differences of up to three orders of magnitude obtained from diodes and FETs, based on asymmetric polymer A, originates from the different charge-density regimes in these two types of devices. One could argue that the experimental mobility versus density in Ref. 23 exhibits a gap at the density range of \(10^{22} \text{m}^{-3}\) thereby hindering a direct comparison between the FET and hole-only diode mobilities. However, we have recently demonstrated that the enhancement of the SCLC hole current in polymer A at high bias at room temperature is entirely due to the carrier-density dependence of the hole mobility. As a result, the observed dominance of the density dependence of the mobility on the SCLC enabled us to determine the mobility-density relation directly from the \(J-V\) characteristics over the full voltage range, as shown in Fig. 7. The experimental SCLC and FET mobilities adjust very well and now nearly cover the whole density range. This agreement clearly proves that for disordered polymers SCLC and FET data can be directly compared.

We now compare the mobility results for polymer E obtained in a hole-only diode and a field-effect transistor as functions of charge-carrier density for three solvents: toluene and chlorobenzene. The experimental hole mobility is plotted in Fig. 8 in the charge-carrier density range of \(10^{15}-10^{20} \text{cm}^{-3}\). The mobility values obtained from the toluene solution show a smooth connection between hole-only and FETs data, showing that the charge transport is three-dimensional (3D)-like. The width of the exponential density of states (DOS) \(T_0\), which is an indication for the energetic disorder in the polymer, is 390 K. In contrast, for the chlorobenzene solution the mobility behavior in Fig. 8 clearly shows a lack of correlation between diode and field-effect transistor measurements. Furthermore, by using chlorobenzene also the width of the exponential DOS decreases to \(T_0=340 \text{ K}\). The explanation is that in the case of toluene the polymeric network is more disordered than in chlorobenzene and the charge transport approaches a 3D-like behavior. The chlorobenzene, on the other hand, evaporates more slowly...
from the spin-coated film, and the polymer chains at the interface with the substrate have more time to rearrange. Apparently, the packing of the polymer network is more favorable for the charge transport in the directions parallel than perpendicular to the substrate mobility data, leading to an increased anisotropy between hole-only diodes and FETs. Thus, dependent on the solvent, the anisotropy in the charge transport can be strongly enhanced.

The anisotropy of the charge transport is a characteristic of high mobility polymers: for example, Sirringhaus et al. demonstrated that self-organization in P3HT results in a lamella structure, which can orient parallel or perpendicular to the substrate, as a function of processing conditions and leads to mobility at very high fields up to 0.1 cm²/Vs. As a result of this different orientation the anisotropy in mobility was found to be more than a factor of 100. We observe a similar behavior in our high-mobility symmetric PPV polymers when chlorobenzene is used as a solvent. In Fig. 9 the mobility of polymers E and J are presented for hole-only diodes and FETs. We observe that an increase of the FET mobility is accompanied by an increase of the anisotropy. This is a strong indication that the use of specific solvents and annealing procedures in the symmetric PPVs result in a better ordering of the film at the semiconductor/insulator interface, thereby enhancing the in-plane transport.

IV. CONCLUSIONS

In conclusion we have presented the influence of the processing and chemical structure of alkoxy-substituted PPVs on the charge-carrier mobility of the field-effect transistor and hole-only diode. It has been demonstrated that by changing the chemical structure of the PPVs the mobility in both types of devices increases for the symmetrically substituted PPVs in comparison with the asymmetrically substituted ones. This is attributed to the increase in the regularity and decrease of the energetic disorder of the polymeric network. Upon annealing of the FET the asymmetrically substituted PPVs showed little improvement, while the field-effect mobility of symmetrically substituted ones can be strongly improved. The use of different solvents has shown a variation in the mobility determined from both hole-only diodes and field-effect transistor for the symmetric PPVs, but not for asymmetric ones. While the transport in asymmetric polymers is isotropic, the anisotropy of charge transport in symmetric polymers is dependent on the solvent. We have demonstrated that optimization of chemical structure, annealing, and solvent leads to high mobility of 9×10⁻⁶ cm²/Vs in the hole-only diode and 1×10⁻² cm²/Vs in FET.

ACKNOWLEDGMENTS

One of the authors (C.T.) wishes to acknowledge the financial support from Dutch Polymer Institute (Project No. 276. We would like to thank B. de Boer for the useful discussions and M. Mulder for the technical support.


FIG. 8. Experimental hole mobility vs hole density for polymer E as determined from hole-only diode (h=120 nm) and field-effect transistor (W =2.5 mm; L=10 μm). The polymer films were spin coated from toluene (closed symbols) and chlorobenzene (open symbols).

FIG. 9. Experimental hole mobility vs hole density for polymers E and J as determined from hole-only diode (h E=120 nm; h J=115 nm) and field-effect transistor (W =20 nm; L=10 μm). The polymer films were spin coated from chlorobenzene.