Organic field effect transistors from triarylamine side-chain polymers

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(Received 2 August 2009; accepted 3 December 2009; published online 17 February 2010)

We present a comparative study of organic field effect transistors (OFET) based on amorphous side-chain p-type polymers obtained from controlled radical polymerization. The side-chain moieties consist of different triarylamines such as triphenylamine, dimethoxytriphenylamine, and dimethoxytriphenyldiamine (DMTPD). The DMTPD-based polymer shows the highest OFET performance with mobilities of 10^{-4} cm²/V s. Furthermore, we show that the electrical properties are independent of the molecular weight due to the all-amorphous character of these side-chain polymers. © 2010 American Institute of Physics. [doi:10.1063/1.3300464]

Materials based on triarylamines (TAA) are a major class of hole conductors in the field of organic electronics. Well-defined, low molecular weight materials, as well as polymers have been developed for various applications. Originally, they were used for xerographic applications,² but recently it was extended to organic light emitting diodes,³ bulk heterojunction solar cells⁴ and solid state dye sensitized solar cells.⁵ In view of their respective applications, the highest occupied molecular orbital level (HOMO) can be chemically tuned via substitution with electron-rich or electrondeficient groups. Furthermore, the physical properties such as crystallinity, solubility, melting temperature, or glass transition temperature can be controlled at the same time. One major parameter that is inherently important for all electrooptical applications is the charge carrier mobility. High charge carrier mobilities for this class of materials have been reported for amorphous low molecular weight derivatives at 10^{-2} cm²/V s using time of flight (TOF) measurements.6

Amorphous polymers often show a low charge carrier mobility since a strong cooperative intermolecular interaction is disturbed and a large energetic disorder is prevalent.⁷ This is not necessarily the case for polytriarylamines, where the low molecular weight materials and the polymers exhibit appreciably high mobilities in their amorphous state.¹ Polymers comprised of TAA were demonstrated with the TAA moiety as part of the conjugated main-chain,⁸ nonconjugated main-chain,⁹ or side-chain.^{10–12} Side-chain polymers are rather comparable to their low molecular weight analogs in terms of the electronic properties, but they possess a high solubility and the mechanical and thermal properties of a polymer. For such materials, the molecular weight is not expected to have a large influence on the electronic properties, which is in contrast to semicrystalline conjugated polymers such as poly(3-hexylthiophene).¹³

There are various methods to access the electrical properties of a material. The charge carrier mobility can be measured for example by TOF,^{2,14} dark injection space-chargelimited current,¹⁵ or in organic field effect transistors (OFETs).

Here we report on OFETs with a series of differently substituted amorphous side-chain poly(triarylamines). In addition, we show that the molecular weight does not influence the charge carrier mobility due to the amorphous nature of the polymers. The synthesis of the TAA polymers is reported elsewhere.^{11,12,16} We investigated three different polymers, poly(vinyltriphenylamine) (PvTPA), namely, poly(vinyldimethoxytriphenlyamine) (PvDMTPA), and poly(vinyldimethoxy-triphenlydiamine) (PvDMTPD) [Fig. 1(a)-1(c)]. Table I shows the physical and thermal properties of these polymers. All the polymers are amorphous and have a glass transition temperature ranging from 130 to 175 °C. PvTPA has a HOMO level of 5.24 eV, which decreases to 4.96 eV for PvDMTPA and PvDMTPD as determined earlier by cyclic voltammetry.¹⁶

We processed OFET devices in a bottom gate bottom contact geometry [Fig. 1(d)] and compared the resulting device characteristics. The charge carrier mobility μ can be extracted in the saturation region of the transfer characteristics as

$$I_{\rm d} = \frac{W}{L} \mu_{\rm sat} C_{\rm i} (V_{\rm g} - V_{\rm th})^2,$$

where W is the gate width, L the gate length, $C_i = 17 \text{ nF/cm}^2$ the silicon oxide capacitance and V_{th} the threshold voltage. The transistor substrates were prepared



FIG. 1. Molecular structures of the polymers, (a) poly(vinyltriphenylamine) PvTPA, (b) poly(vinyldimethoxytriphenylamine) PvDMTPA, (c) poly(vinyldimethoxytriphenlydiamine) PvDMTPD, (d) schematic of a bottom gate bottom contact OFET architecture.

96, 073503-1

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TABLE I. Material properties and OFET results for PvTPA, PvDMTPA, and PvD-MTPD.

	PvTPA	PvDMTPA	PvDMTPD
$\overline{M_{\rm n}}$ (kg/mol)	15.8	23.6	22.4
T_{σ} (°C)	143.6	146.2	174.5
HOMO (eV) ^a	5.24	4.96	4.96
$\mu_{\rm sat}$ as spun (cm ² /V s)	1×10^{-7}	3×10^{-5}	1×10^{-4}
V _{th} as spun (V)	-45.1	-4.3	-4.1
on/off spun	4×10^{1}	2.5×10^{2}	1.6×10^{3}
$\mu_{\rm sat}$ annealed (cm ² /V s)	3×10^{-5}	5×10^{-5}	1×10^{-4}
$V_{\rm th}$ annealed (V)	-35.2	-13.2	-12.1
on/off annealed	6×10^{2}	4.0×10^{2}	2.3×10^{3}
W/L	$10 \text{ mm}/10 \mu\text{m}$	$10 \text{ mm}/10 \mu\text{m}$	$10 \text{ mm}/7.5 \mu\text{m}$

^aReference 16.

and silanized with hexamethyldisilazane according to published procedures.¹⁷ The polymers were spin cast from a 1.9 wt % toluene solution. This procedure and all subsequent device annealing and device characterization steps were carried out in a glove box under inert gas atmosphere. The transistors were characterized using a HP4155A and a HP4156B semiconductor parameter analyzer.

The as spin-cast samples of PvTPA showed a very weak performance, with high threshold voltages, small on-off ratios and low charge carrier mobilities. Annealing the sample at approximately 15 °C above its T_g caused a significant increase in the performance leading to greater than tenfold drain currents and a charge carrier mobility of around 3 $\times 10^{-5}$ cm²/V s. The threshold voltage was still quite high at -37 V. The output and transfer characteristics are shown in Fig. 2. The polymers PvDMTPA and PvDMTPD, each carrying two methoxy groups showed a different behavior. After spin-coating, both the PvDMTPA and the PvDMTPD showed a significantly better performance compared to PvTPA, which did not improve significantly after thermal annealing above T_{g} . Both materials showed low threshold voltages between -4 to -5 V. Annealing shifted the threshold voltage to higher values of -12 to -13 V. We assume this due to conformational changes in the polymer and an altered spatial ordering of the polar methoxy groups toward the gate dielectric. The PvDMTPD was superior in terms of its charge carrier mobility and on-off ratio. The PvDMTPA

had mobility $\mu_{sat} = 1.2 \times 10^{-4} \text{ cm}^2/\text{V} \text{ s}$ and an on-off ratio 10³. The superior charge carrier mobility of PvDMTPD is in line with previous findings on the solar cell performance of poly(triarylamine) based block copolymers.¹⁶ Furthermore, the contact resistance of PvDMTPA and PvDMTPD was very low, whereas PvTPA showed a significant contact resistance, as can be seen in the slow rise of the output characteristics. We tentatively propose that spatial ordering of the methoxy groups at the dielectric interface might cause the difference in contact resistance. Changes in the OFET performance before and after annealing have generally been attributed to morphological and spatial ordering, but also to changes in the energetic disorder at the interface introduced by local polarization.¹⁸ The latter possibility can be rather excluded since the interface itself stays unaffected. The dimethoxy groups seem to have an effect after annealing as both materials show a significant increase in their threshold voltage. The polar methoxy groups may conform to the dielectric interface in such a way, that a significant increase in the threshold voltage is induced. This is not observed in pure PvTPA which contains no substituents. Here, a large contact resistance is observed, that affects the overall extracted charge carrier mobility.¹⁹

The increase in performance of PvTPA after annealing may be related to a better packing of the triphenylamine moieties and the higher degree of freedom that is conserved with unsubstituted triphenylamine moieties. Low molecular weight TPA without substituents shows a strong crystallinity.²⁰ The introduction of substituents rather supports the formation of an amorphous phase. In the case of the side chain poly(vinyltriarylamines) presented here, only amorphous states have been observed. The reason for that is the nonplanar conformation of the TPA core that hinders a crystalline packing when attached to a polymer backbone. PvDMTPA and PvDMTPD contain much bulkier side groups compared to PvTPA which is a possible explanation for the only minor changes in charge transport before and after annealing. Therefore, changes upon annealing are rather expected at unsubstituted triphenylamine side chains-where the small molecule counterpart shows an extensive crystallinity.



FIG. 2. [(a)-(c)] The upper graphs show the output characteristics with $V_g=0V$ to -60 V in steps of -10 V. [(d)-(f)]. The bottom graphs show the transfer characteristics of PvTPA, PvDMTPA, and PvDMTPD for $V_{ds}=-60$ V. The black lines correspond to the as spun polymers and the gray lines to the annealed transistors. The dashed lines show the first derivative $\partial \sqrt{I_d} / \partial V_G$ in units of the charge carrier mobility as calculated from the saturation region.

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FIG. 3. (a) Charge carrier mobility of PvDMTPA as a function of the molecular weight. Black squares show as spun transistors and the gray circles show the mobilities for annealed transistors. (b) Glass transition temperature T_g of PvDMTPA as a function of the molecular weight. The gray curve shows an asymptotic fit according to Fox and Flory. The T_g for M_w =11.5 kg/mol shows a certain inconsistency due to a double peak in the tan(δ) curve (see supplementary information S2) Ref.23.

In order to study the effect of the molecular weight on the device performance, we prepared OFET devices using a PvDMTPA series with different molecular weights. The PvDMTPAs with well-defined molecular weights between 3 and 30 kg/mol and fairly low polydispersities between 1.1 and 1.2 were used. As shown in Fig. 3, the charge carrier mobility of PvDMTPA of around 10^{-5} cm²/V s does not change with molecular weight within the margin of error. This is different from the case of conjugated polymers, where the polymer chain length has a direct influence on the electronic properties.¹³

These amorphous polymers have the advantage of unchanged electronic properties, while the physical properties such as the glass transition temperature T_g , do scale with molecular weight. Figure 3(b) shows the T_g as a function of the molecular weight. We determined the T_g by dynamic mechanical analysis (DMA) measurements using a Triton DS6000 Thermal Analyzer. The T_{gs} were determined as the peak value of $tan(\delta)$ at an actuation frequency of 1 Hz, where δ is the phase difference between the store modulus G' and the loss modulus G''.²³ This method for determining T_{σ} results in slightly higher values compared to differential scanning calorimetry measurements, but the extraction of the $tan(\delta)$ peak value was very reliable for small amounts of polymers.²¹ In agreement with Fox and Flory,²² the glass transition temperature shows an asymptotic behavior as follows: $T_g = T_{inf} - K/M_n$, where we found $T_{inf} = 148.2$ °C and $K = 70.8 \times 10^5$ g/mol. The T_g varies from 125 °C for the lowest molecular weight of 2900 g/mol to a saturation value at around 145 °C for polymers with more than 20 kg/mol. Thus, by varying the molecular weight, it is possible to adjust the physical properties to the needs of the processing

conditions without changing the electronic properties.

To conclude, we have investigated the charge carrier mobilities of side-chain TAA polymers PvTPA, PvDMTPA, and PvDMTPD with differently substituted TAA units. PvD-MTPD bearing triphenyldiamine units demonstrated the best performance in terms of charge carrier mobility, threshold voltage, and on-off ratio. Furthermore, we used PvDMTPA as an example to show that the charge carrier mobility is independent of the molecular weight while the thermal properties are not. The independence of the molecular weight is different to conjugated polymers such as polyhexylthiophene, where the molecular weight influences the conjugation length but also morphological properties such as the formation of crystalline domains together and the interconnectivity of those. Thus, they offer an excellent possibility to adjust the glass transition temperature through the molecular weight and also take a direct influence on the phase separation when blended with an acceptor material.

We acknowledge the financial support from the European network "PolyFilm" under Grant No. RTN-6 and the DFG under SFB 481. S.H. thanks Universität Bayern e.V. for the scholarship of the Bayerische Graduiertenförderung.

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