Enhanced Mobility of Poly(3-hexylthiophene) Transistors by Spin-Coating from High-Boiling-Point Solvents

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Chloroform is a general solvent for poly(3-hexylthiophene) (P3HT) active layers in field-effect transistors. However, its low boiling point and rapid evaporation limit the time for crystallization during the spin-coating process, and field-effect mobilities achieved for P3HT films spin-coated from chloroform are typically on the order of 0.01 $cm^2/(V\ s)$. Here we investigate a range of solvents with higher boiling points. We find that 1,2,4-trichlorobenzene with good solubility and a high boiling point significantly improves the field-effect mobilities up to 0.12 $cm^2/(V\ s)$ with on:off ratios of 10^6. By controlling the microstructure through the choice of solvent while keeping the molecular weight fixed, we observe a clear correlation between the field-effect mobility and the degree of microcrystalline order as measured by X-ray diffraction, as well as the strength of polaronic relaxation of charge carriers in the accumulation layer as measured by optical spectroscopy of field-induced charge.

Thin-film transistors based on solution-processed semiconducting conjugated polymers have interesting technological attributes, such as compatibility with simple direct-write printing techniques, general low-cost manufacturing approaches, and flexible plastic substrates.[1−3] To date many soluble materials have been proposed, but only a few can truly realize the high mobilities required for organic circuits that have adequate performance for applications such as active matrix displays or low-cost intelligent labels. Poly(3-hexylthiophene) (P3HT) is of particular interest due to its self-organizing properties to form a microcrystalline structure. Intensive research toward improving its mobility has shown that the microstructure in P3HT is critically affected by regioregularity (RR)[4] and molecular weight (MW),[5] resulting in variations of the field-effect mobilities by several orders of magnitude. High field-effect mobilities of 0.1 $cm^2/(V\ s)$ have been further demonstrated through the optimization of device preparation, such as choosing appropriate solvents,[6] dielectric treatments,[7] and deposition methods.[8]

It has been claimed that a high MW is a more important factor for achieving high mobilities than the degree of crystallinity.[5] Lower MW polymers resulted in lower mobilities than higher MW material ($\mu = 0.01$ $cm^2/(V\ s)$) despite a higher degree of crystallinity for the lower MW samples. This has been attributed to better interconnectivity of the polymer network in higher MW samples; however, a clear separation of the effects of microcrystalline order and molecular weight is still missing. We present here a study of the electronic properties of P3HT films with a fixed, sufficiently high molecular weight, and study systematically their electronic properties as a function of the degree of microcrystalline order as controlled by the boiling point of the solvent from which the P3HT film is deposited.

For the widely used spin-coating process significantly lower mobilities are usually found as compared with solution-cast deposition.[6,8] This is closely related to the limited time available for chain alignment forced by the rapid drying of solvent. Here we find that, by using higher boiling point solvents instead of chloroform for spin-coating, P3HT transistors with mobilities higher than 0.1 $cm^2/(V\ s)$ and large on:off current ratios of 10^6 can be achieved. Because the slower solvent evaporation speed facilitates the growth of a highly crystalline film, interchain interactions become stronger and thus improve the electroconductivities significantly. Our obser-

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vations not only suggest an elegant and reproducible way to control the ordering in P3HT, but also provide further insight into the device physics of P3HT FETs and the origin of high mobilities.

Regioregular P3HT (MW = 37 K, RR ≈ 98%) used in this study was obtained from Merck Chemicals Ltd., Southhampton, U.K. Several solvents with different evaporation rates were investigated, including chloroform, thiophene, xylene, cyclohexylbenzene (CHB), and 1,2,4-trichlorobenzene (TCB). All the solutions were prepared at a concentration of 10 mg/mL, and heated at 70 °C for 30 min before being filtered through a 0.45 μm pore size PTFE membrane syringe filter. In general, thiophene and TCB can dissolve P3HT as easily as chloroform, whereas xylene and CHB have fairly poor solubilities, and continuous heating is required after the solutions are filtered to avoid aggregation and gelation. (The shelf life of chloroform, thiophene, and TCB solutions can be longer than one week, but xylene and CHB solutions gel after several hours at room temperature.) The transistors for solvent studies were made with a bottom-gate top-contact configuration. The substrate, heavily n-doped silicon as gate contact with 200 nm thermally grown SiO_2 dielectric, was first treated with hexamethyldisilazane (HMDS) or 1*H*,1*H*,2*H*,2*H*-perfluorodecyltrichlorosilane (FDTS) for controls. As a result the dielectric surface became hydrophobic after HMDS treatment and oleophobic after FDTS treatment. 200−600 Å thick P3HT films were then spin-coated at 1500 rpm onto the substrates, and annealed at 100 °C for 10 h under vacuum to remove the residual solvent and unintended doping. The source and drain contacts were finally made by evaporating a 40 nm thick gold layer on top of the P3HT layer. All solution preparation, device-making, and $I-V$ measurements were performed in a N_2 atmosphere.

Figure 1 shows the transfer characteristics of P3HT transistors spin-coated from various solutions on HMDS-treated (a) and FDTS-treated (b) dielectric, respectively. For HMDS-treated substrates all devices turn on approximately at $V_g = 0$ (except for the devices coated from thiophene solution, which exhibited serious dewetting issues such that no operational devices could be fabricated). In the FDTS devices the turn-on voltage is shifted to more negative values indicative of a permanent electric field at the interface.[9] The saturated field-effect mobilities are extracted by using the same analysis as in ref 5. The insulator capacitance $C_{ox} = 16.9$ nF/cm^2 is for a 200 nm thick SiO_2 insulator, and the device channel width W and length L are 1.5 mm and 95 μm, respectively. The results summarized in Table 1 clearly show that the field-effect mobilities vary significantly dependent on the boiling points of the solvents. For both HMDS and FDTS treatments the devices made by chloroform have the lowest mobilities. The result differs to some degree from the data published by Z. Bao et al.,[6] who reported mobilities of ~9 × 10^{-3} cm^2/(V s) in films spun from chloroform, which are more than 100 times higher than those in films spun from xylene. (Their highest mobilities up to 0.045 cm^2/(V s) were obtained in solution-cast films.) A possible reason for this might be a higher level of extrinsic doping in the polymer used in ref 6. Doping tends to reduce the solubility of P3HT in certain organic solvents. Here we use carefully purified P3HT for which the solubility in xylene and CHB can be enhanced by heating of the solution to a degree that it renders mobilities higher than those of chloroform or thiophene (see the FDTS case). This indicates that the boiling point of the solution is a critical factor for the polymer crystallization process, as reported for solution-cast films.[10]

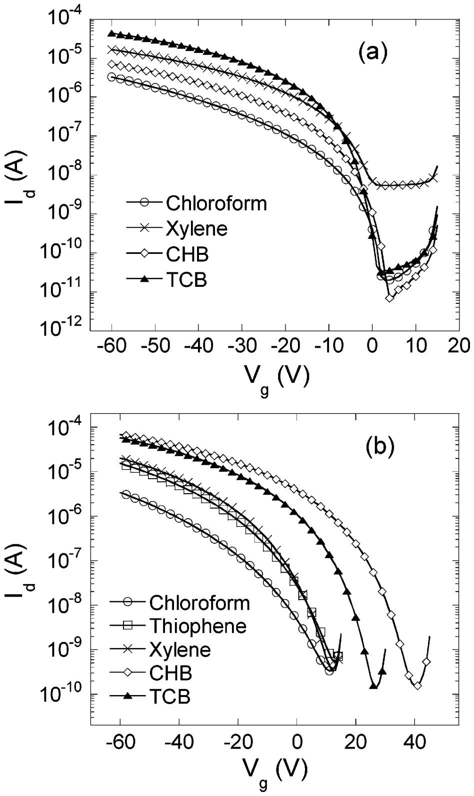

Figure 1. Transfer characteristics of P3HT transistors spin-coated from different solvents on (a) HMDS- and (b) FDTS-treated dielectric surfaces, where $V_{ds} = -60$ V. Thiophene cannot be the solvent for the HMDS-treated surface due to its dewetting properties.

We observe a larger off current in the xylene devices (see Figure 1a), which might occur due to the aggregates formed in relatively poor solvents that tend to lower the ionization potential and facilitate extrinsic doping effects, or could be related to residual impurities, and oxidative doping by the solvent. Overall, the best performance can be found in devices made by TCB. The mobility up to 0.12 cm^2/(V s) in HMDS treatment is believed to be the highest value reported so far for a spin-coated P3HT transistor, almost 10 times higher than that using chloroform in the same process. We believe that such improvements are not only because of a good solubility in TCB, but more likely due to the extremely high boiling point (219 °C), which makes a solvent-rich polymer thin film after 1 min of spinning. For both TCB and CHB (which has a higher boiling point, but poorer solubility than TCB) it takes 5−10 min for the film to dry, while spin-coated films from chloroform (or thiophene and xylene) would dry within a few seconds of spinning. Thus, the molecules in TCB

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Table 1. Transistor Parameters (Mobility, On:Off Ratio, and Subthreshold Slope) for the Different Solvents in Figure 1, Together with Their Boiling Points

		HMDS			FDTS		
	bp (°C)	mobility (cm^2/(V s))	I_{on}/I_{off}	subthreshold slope (V/dec)	mobility (cm^2/(V s))	I_{on}/I_{off}	subthreshold slope (V/dec)
chloroform	60.5−61.5	0.012	10^5	2.45	0.0076	10^4	9.1
thiophene	84				0.030	10^4−10^5	6.5
xylene	138−139	0.042	10^3−10^4	5.5	0.041	10^5	5.1
CHB	239−240	0.022	10^6	1.8	0.049	10^5−10^6	4.25
TCB	218−219	0.12	10^6	1.7	0.063	10^5−10^6	3.8

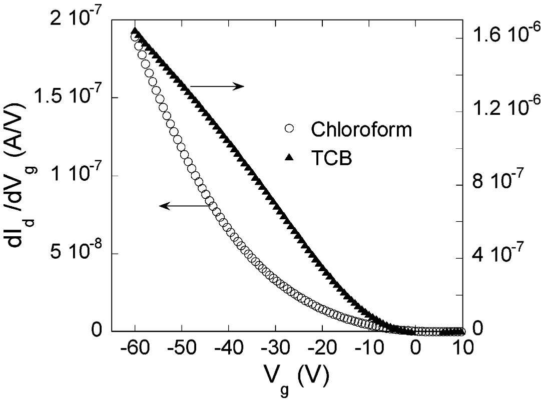

Figure 2. Transconductance dI_d/dV_g of the HMDS-treated devices made by TCB and chloroform, the same as those in Figure 1a (V_{ds} = −60 V).

can self-organize over a long time to form the thermodynamically favored structure, which is the orientation reported for solution-cast films.[10,11] It thus appears that with the semidry film resulting from the spin-casting with high-bp solvents, the dry film tends to combine the homogeneity of the spin-cast films with the internal structure of a solution-cast film.

Indeed, as seen in Figure 2, a better structural order in TCB devices manifests itself as a linear dependence of transconductance dI_d/dV_g on V_g above the threshold voltage V_t. This implies that the mobility in the TCB devices is independent of the gate voltage, while in the chloroform devices the mobility increases with increasing carrier concentration in the channel, indicating the presence of a larger number of electronic defect states effectively trapping the carriers at small carrier concentration. Similar observations have been made in high-mobility P3HT and a-Si transistors.[7,12] A superlinear dI_d/dV_g versus V_g relationship in the chloroform device reflects the charges prevalently trapped in localized states owing to the more disordered structure.

Figure 3 shows the X-ray diffraction of thin films made by the same processing method as used for HMDS-treated transistors. The grazing incidence diffraction experiments were carried out on the *z*-axis diffractometer at BW 2, Hasylab, using a wavelength of 1.2398 Å. The fixed, grazing incidence angle was 0.16° for the in-plane measurements and was offset from the normal by 0.3° for the out-of-plane measurements. The scattered intensity was measured with a point detector. A highly crystalline structure with preferential orientation is demonstrated throughout the thin film spun from TCB. The interdigitated side chains tend to be oriented perpendicular to the substrate and the π-stacked conjugated lamellae parallel to the substrate, providing an efficient pathway for in-plane charge transport.[4] The preferential orientation of the microcrystalline domains in spin-coated TCB films is the same as that generally obtained in solution-cast films.[10,11] By contrast, the films spun from chloroform appear less crystalline. The intensity of the in-plane π−π stacking diffraction is much weaker than that of the corresponding diffraction in the TCB films. Although the overall preferential orientation of the microcrystalline domains in chloroform films is the same as that of the TCB films, the lower mobilities are interpreted as being the result of less efficient interchain stack formation as a result of the shorter drying time. In a previous study of spin-cast films of regioregular P3HT with a MW of ~87 000,[11] no dependency of the solvent was found. We suggest that this is due to the different molecular weight and surface treatment employed there.

This is supported by atomic force microscopy (AFM) performed on films prepared under the same conditions as the FET devices from TCB and chloroform solutions (Figure 4). For TCB the AFM measurements are capable of resolving well-defined nanoribbons with a length of several micrometers, a diameter in the plane of the film on the order of 30−50 nm (as measured by AFM and electron microscopy), and an apparent height in AFM on the order of 3−5 nm. In contrast, the films prepared from chloroform solution appear less crystalline, and have a granular surface topography without apparent crystalline structures. Note that in ref 5, where chloroform was used as a solvent, the needlelike morphology was only observed in films of low molecular weight.

Optical spectroscopy of field-induced charge was utilized to obtain a more microscopic understanding of the electronic properties of the polaronic charge carriers, and the observed correlation between microstructure and mobility. The measurements were performed using the same device configuration as that of the FET devices by comparing mid-infrared spectra with the gate bias at V_g = −30 V and V_g = 10 V. The spectroscopic feature accessible in this spectral range is the broad continuum of charge-transfer (CT) transitions between the charged and neutral molecules. The CT transition is somewhat analogous to the Drude absorption observed in good metals,[13] and has previously been shown to be very sensitive to the presence of interchain interactions.[14,15] We observe (Figure 5) that the TCB device has more intense CT transitions below 0.5 eV and more intense (anti)resonance vibrational transitions below 0.2 eV.[14,15] Although the spectral range of our experimental setup does not allow measurements below 50 meV, it is clear

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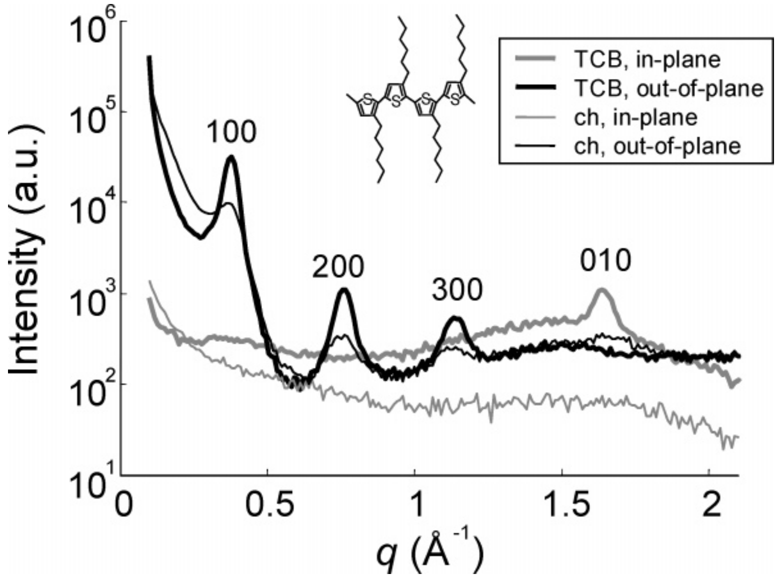

Figure 3. Grazing incidence X-ray diffraction measurements for P3HT thin films spin-coated from TCB and chloroform on HMDS-treated substrates, with out-of-plane and in-plane scattering geometry. The (100), (200), and (300) plane reflections are due to the lamellar layer structure, and the (010) reflection is due to $\pi-\pi$ interchain stacking. Note that the π-stack signal at 1.65 Å^{-1} is missing in the chloroform sample. The evident difference of the (010) peak between two samples confirms the influence of interchain interaction on mobilities.

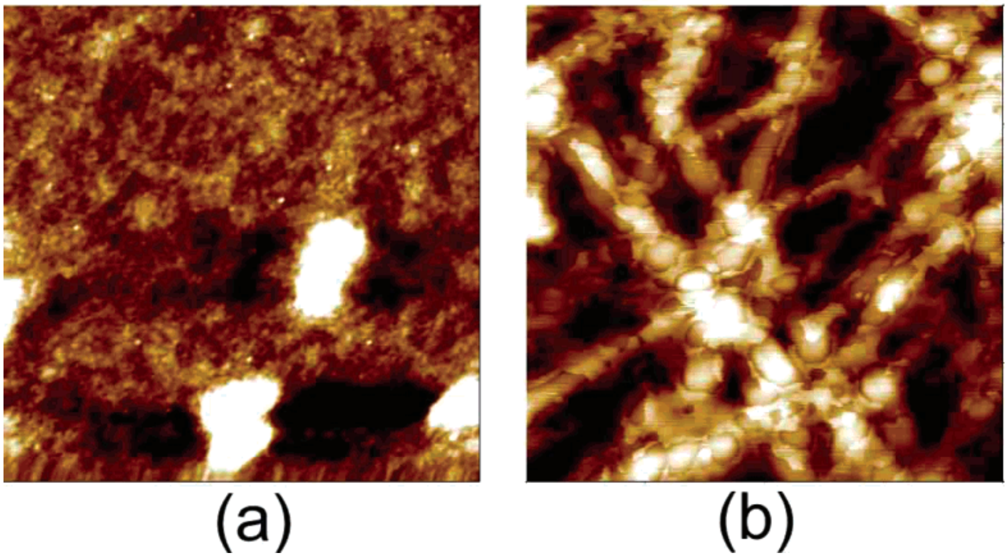

Figure 4. Tapping-mode AFM images of P3HT made by (a) chloroform and (b) TCB. The films were spin-coated from the same solutions used for FETs onto Spectrosil substrates. The image size is 1 μm × 1 μm, and the vertical scale is 6 nm. Some isolated clusters possibly due to polymer aggregates can be seen in the chloroform film.

from Figure 5 that the peak of the CT transition for the TCB device occurs at an energy lower by at least 50 meV than that of the chloroform device. This is direct spectroscopic evidence for the more pronounced interchain interaction in TCB devices. These findings combined with the above X-ray measurements provide firm evidence of stronger interchain interactions resulting in reduced polaronic relaxation energies being responsible for the improved mobilities for P3HT films coated from higher boiling point solvents. This is in agreement with previous findings.[4]

In ref 5 it has been found that lower MW polymers result in lower mobilities than higher MW material ($\mu = 0.01$ cm^2/(V s)) despite a higher degree of crystallinity for the lower MW samples, while earlier studies showed the importance of a high regioregularity, and associated high degree of crystallinity, to obtain high mobilities. To clarify the role of these different factors, in the present study we have used P3HT with a fixed MW similar to the high MW samples used in ref 5 and high regioregularity of RR $\approx$ 98%, and varied the degree of microcrystallinity by the choice of solvent. Our results clearly demonstrate that, for polymers of a fixed and sufficiently high MW, mobilities can be much improved from 0.01 to 0.1 cm^2/(V s) with a higher degree of crystallinity and stronger in-plane-oriented $\pi-\pi$ stacking. It is possible that by further careful optimization of both MW and polymer processing even higher mobilities could be achieved.

In conclusion, by utilizing high-boiling-point and high-solubility solvents, spin-coated P3HT transistors with high mobilities of >0.1 cm^2/(V s) and on:off current

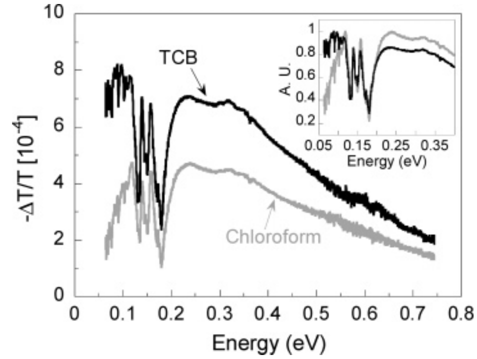

Figure 5. FTIR charge modulation spectra for HMDS-treated P3HT transistors made by TCB and chloroform. The spectrum was extracted from the difference of infrared transmission spectra with the FET device being dc-biased alternately in the accumulation ($V_g = -30$ V) and depletion ($V_g = 10$ V) regimes. The normalized transmission in the inset illustrates the difference in peak positions for the two devices.

ratios of 10^6 have been demonstrated. The microstructure in such devices is highly crystalline with a needle-like morphology, and efficient interchain stacking parallel to the in-plane current flow. The use of appropriate solvents with high boiling points for spin-coating combines the advantages of increasing the drying time similar to that of solution-casting while retaining a high thin-film uniformity. This processing is not only simpler to reproduce than solution-casting but more applicable to fabricate large-area or multilayer polymer devices.[16]

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