Synthesis, Material Properties, and Transistor Performance of Highly Pure Thiophene Oligomers

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Studies of thiophene oligomers are driven by potential applications in nonlinear optical[1] and electroluminescent[2] devices, and in semiconductor-based components including Schottky diodes[3] and thin-film transistors (TFTs).[4] In some respects, such as dopant-induced conductivity, the electronic behavior of oligomers higher than the tetramer is like that of the much less processable polythiophene,[1ab,5] so that one can take advantage of the film forming capability of the oligomers. The TFT application is particularly exciting at present because of the possible use of organic semiconductor devices in flexible circuits constructed on plastic substrates at processing temperatures below those normally required for amorphous silicon-based electronics.[6] In this paper, we describe improved methods for the synthesis and refinement of α-6T, α-4T, and α-8T. Use of the specially purified material in transistors with silicon oxide dielectric layers leads to unprecedented on/off ratios well in excess of 10^6 for the hexamer (over an 80 V range in gate voltage) and mobilities above 0.01 $\mathrm{cm^2/V\ s}$ for the hexamer and octamer.

The unique characteristics of TFTs based on α-6T as the semiconductor have been well documented through the pioneering efforts of Francis Garnier and his collaborators.[7] Recently, the possibility of improving these devices by end substitution of α-6T has been raised.[8] A 25-fold increase in mobility was attributed to replacement of the terminal hydrogens with hexyl groups and thereby improving the organization and continuity of the semiconductor film. In our work, we have focused on synthetic procedures aimed at producing the parent compound free of any electronically or morphologically important contaminants. Thus, we are able to apportion contributions to mobility arising from improved material purity, chain length, and terminal substitution.[9]

Synthesis and Purification. The two modern methods of preparing α-6T from α-terthienyl (α-3T) are to oxidatively dimerize the trimer with ferric chloride in benzene[10] and to couple 2 equiv of the 2-lithio derivative of α-3T with cupric chloride.[11] The former method gave us an extremely dark crude product that contained 2% Fe (as ferrous chloride) by elemental analysis and has been reported to cause conjugation defects through β-coupling.[7a] The latter method is cleaner in that less metal is incorporated, but in our hands, recrystallized product contained 0.77% Cl and only 0.033% Cu, evidence of chlorinated α-6T contaminants that would be almost impossible to remove. The use of cupric chloride in the oxidative dimerizations of lithiated α-2T and ω-hexyl-α-3T also led to extensive chlorination, up to 25%. The addition of TMEDA to the reaction mixture suppressed but did not prevent this chlorination.

An alternative organolithium coupling reagent whose residues are easier to remove and which does not cause side reactions is ferric acetylacetonate.[12] Use of this reagent to convert lithiated, TMEDA-free α-3T in THF solution to α-6T and extensive purification of the crude product by washing with dilute HCl and water, digestion with dilute aqueous Na_2CO_3 and a series of hot solvents ranging in polarity from water to toluene, recrystallization from mesitylene under nitrogen with hot filtration, and sublimation along a glass tube[13] under high vacuum produced our transistor-grade material. Similar procedures were followed for α-4T and α-8T. The former was recrystallized from toluene, and the latter from 1,2,4-trichlorobenzene, decanting the recrystallized α-8T suspended in the mother liquor from insoluble residue.

One drawback of ferric acetylacetonate is its lower reactivity relative to cupric chloride. Thus, coupling occurs at a higher temperature, where lithium–hydrogen exchange reactions may occur. In the case of the α-4T synthesis, ca. 10% of α-6T is produced as a contaminant by deprotonation of the product and coupling to unreacted α-2T. Preliminary trials have identified cupric triflate and ferric trifluoroacetylacetonate as possibly superior alternatives in that they are more reactive, but still nonhalogenating.

Although the melting point for an α-6T sample was recently reported as 280 °C,[8a] the generally accepted value is in the range 302–307 °C, determined both by conventional observation and by DSC. Visual observation of the melting of our transistor grade α-6T in air indicates a melting point >305 °C, perhaps as high as 310 °C. DSC (heating/cooling at 10 °C/min) in an inert

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atmosphere is much clearer, with a narrow, reversible transition centered at 313.5 °C. This is 6.5 °C higher than the next highest reported value[15] and 33.5 °C higher than what appears to have been sufficient for a working transistor.[8] Our best DSC trace is only obtained from material which has been recrystallized in an inert atmosphere and sublimed. Various references are made in the literature to recrystallization from polar aromatic solvents, Soxhlet extraction, and sublimation, but the specific sequence used here gives a uniquely pure product. The melting point of our α-4T is 208–210 °C, in agreement with the literature.[16] Our α-8T melts in air in the range 352–357 °C, higher than previously reported,[16] but still over a broad range. The DSC melting transition was even broader, in the range of 340–370 °C.

Performance of α-6T in TFTs. TFTs with 12 μm channel lengths and 250 μm channel widths were fabricated on thermally oxidized, conductive Si substrates. The oxide, serving as the gate dielectric, was 300 nm thick. The gate region was accessed by a gold ohmic contact to the Si, and gold source and drain contacts were lithographically defined on the silicon oxide. The organic semiconductors were then evaporated onto the entire assembly at a pressure of 10^{-6} Torr. TFTs made from incompletely purified α-6T display p-type off-conductivity due to unintentional doping. This is consistent with an earlier conjecture that α-6T is p-type immediately after deposition.[3b] The mobility of the semiconductor in such devices is 0.001–0.01 cm^2/Vs, and the on/off ratio is in the range (1–10) × 10^3, as has been previously observed.[7] The off-current is measured under conditions where the gate is positively biased with respect to the source, thereby depleting some of the residual carriers.

Material which has been purified more carefully shows a different behavior, as shown for the low V_D regime[17] in Figure 1a. The off-current, measured under vacuum, is 10–100 pA, and the on/off ratio is in the range 1–10 million. This grade of α-6T is barely p-type and could almost be considered *intrinsic,* since carrier depletion reduces the off-curent only by a factor of 10. When the material for the evaporator source is selected from the most mobile sublimation fraction, behavior as shown in Figure 1b is observed. Depletion by a positive gate bias is not required to achieve the lowest off-current or to obtain an on/off ratio >1 × 10^6. The magnitude of the off-current is only ca. 20 pA. To our knowledge, this is the first example of an organic semiconductor showing purely intrinsic behavior. Minimizing the off-current in this manner is clearly advantageous in increasing the dynamic response of the TFTs.

Other factors contribute to device performance in additon to material purity, including the flatness and chemical homogeneity of the oxide surface, and a contact geometry that allows for ohmic contacts but does not shadow semiconductor deposition in the gate region.

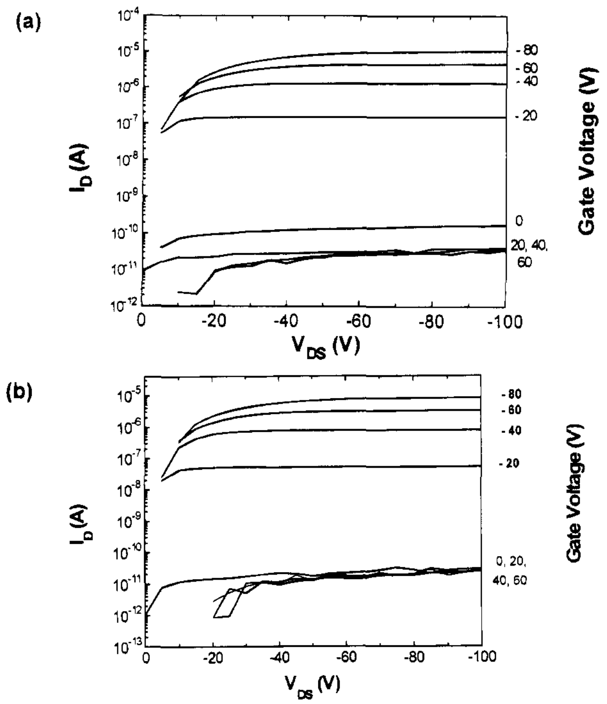

Figure 1. Transistor characteristics for α-6T: (a) the major sublimed fraction; (b) the intrinsic fraction.

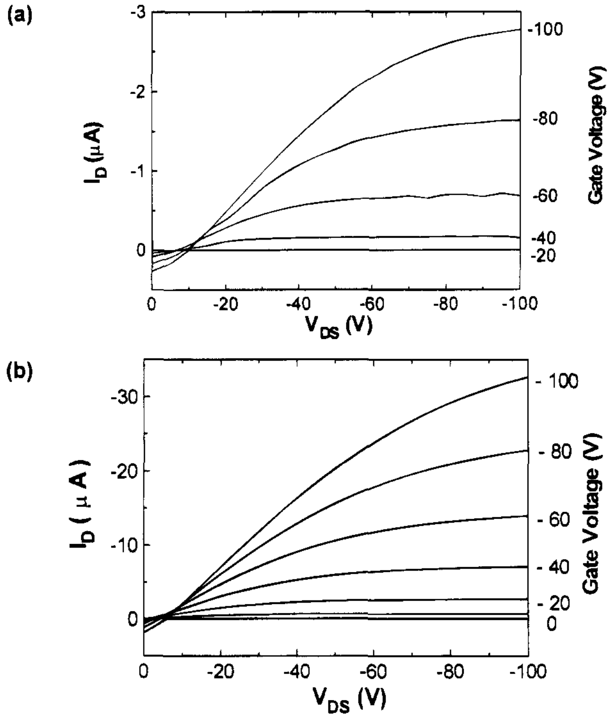

Figure 2. Transistor characteristics for (a) unannealed α-4T, 690 Å, and (b) α-8T, 500 Å, annealed at 150 °C.

Devices made from p-type material are substantially unaffected by light or oxygen, but the intrinsic devices can be made slightly p-type through operation in humid air. Means of protecting the intrinsic devices are under investigation.

α-4T and α-8T TFTs. The mobilities of these compounds prepared by us are in the range 10^{-4}–6 × 10^{-3} for the tetramer and (1–3) × 10^{-2} for the octamer, determined from the device characteristics shown in Figure 2. While both compounds show a wider range of mobilities than does our best α-6T, they are clearly

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[17] We have developed a computer model which fits experimental data in both linear and saturation regions with a single mobility. This model works well for thiophene oligomers and is described in: Torsi, L.; Dodabalapur, A.; Katz, H. E. *J. Appl. Phys.* **1995**, *78*, 1088.

of higher mobility than had been previously thought.[4] In particular, the octamer does not have lower mobility than the hexamer and in fact may be superior to the hexamer in this respect, although the off-current of the octamer is considerably higher than for α-6T. The off-currents at low V_{DS} are due to leakage from the gate to the drain and arise because both the gate and organic active material are unpatterned. We have observed that patterning of the gate contact and/or the active material greatly reduces this leakage current. The off-current in α-4T is very low, typically the same as well-purified α-6T.

Conclusion. Syntheses of rigorously pure thiophene oligomers have been developed. In the case of α-6T, the first demonstration of intrinsic behavior in an organic semiconductor has been realized. The considerations of synthesis, purification, and device design that led to optimal α-6T are probably relevant for its derivatives[8,9] as well. The on/off ratio, current-carrying capacity, and thermal stability of α-6T films have been increased to the point where they are sufficient for use in plastic-based components. By applying these principles to α-4T and α-8T, more accurate comparisons of the mobilities have been made. Future efforts will focus on translating this level of performance to devices made from readily available polymeric substrates and dielectrics. The control of such factors as leakage current through the dielectric and surface inhomogeneities between the dielectric and semiconductor will be significant challenges as the plastic-for-silicon substitution is attempted.

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