Synthesis, Solubility, and Field-Effect Mobility of Elongated and Oxa-Substituted α,ω-Dialkyl Thiophene Oligomers. Extension of "Polar Intermediate" Synthetic Strategy and Solution Deposition on Transistor Substrates

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Our investigation of thiophene oligomers as organic thin film transistor (TFT) semiconductors is extended to the hexamer with dodecyl and octadecyl end-substituents and with side chains containing ethereal oxygens. Two thiophene tetramers are studied as well. All of the new compounds are prepared via polar, monosubstituted half-oligomers that are purified, further elaborated, and dimerized. Properties are reported in comparison with the previously reported dihexyl compounds. All of the compounds form ordered films with orientation perpendicular to the substrate. For the hexamers, the longer chains decrease the TFT mobility of evaporated films, while the oxygens have very little electronic effect, even though the oxygen does cause an approximate doubling of the solubility. A tetramer with an ether side chain has a mobility below 0.01 cm^2/Vs. Films were also cast from dilute solution and showed mobilities at or above 0.01 cm^2/Vs in several cases. This casting process may be useful in devising all-liquid-phase fabrication protocols for organic-based electronic circuits.

The development of printed and plastic-based electronic circuitry for inexpensive low-density logic elements and mechanically flexible display drivers will require thin film transistors (TFTs) with organic or polymeric semiconductors as the active materials.[1] Beginning with the original reports of Garnier on the utility of vacuum-sublimed thiophene oligomers in TFTs,[2] this compound class, exemplified by the linear hexamer (α6T), has been an important vehicle for exploring the transport mechanisms,[3] performance limits,[4] and applications[5] of these devices. The addition of hexyl substituents to the two terminal carbons of α6T leads to improved film ordering[6] and a 2- to 3-fold increase in the mobility (*μ*).[7] Most recently, work on dihexyl-α8T[8] and -α4T[9] has also been described.

The primary economic advantage to organic TFTs will lie in the more facile processing procedures available for organics compared to well-established silicon-based technology. The most attractive deposition and patterning methods are likely to be liquid-based, requiring that the semiconductor and other materials be solution- or melt-processable. In this regard, dihexyl-α6T (DHα6T) is somewhat superior to its parent because of its greater solubility, being recrystallizable from xylene[7] rather than the higher-boiling mesitylene required for α6T itself.[10] The solubility may be further doubled when highly oxygenated substituents are present,[11] although the mobilities of such α6Ts have not been reported. Decreasing the oligomer length to four rings increases the solubility enormously, but this is also believed to decrease the mobility,[12] though not as drastically as was once thought.[10,13]

Our previously described synthetic approach to end-substituted thiophene oligomers relies on a strategy of synthesizing monoalkyl oligomers, of half the length of the intended disubstituted target, via polar monosubstituted intermediates,[7] as shown in Scheme 1. The intermediates are chromatographically separable from starting materials and disubstituted byproducts and

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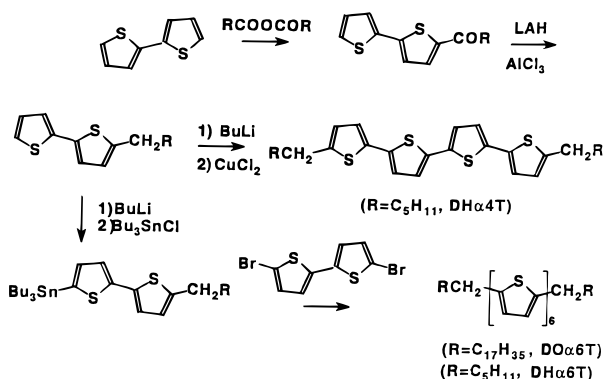
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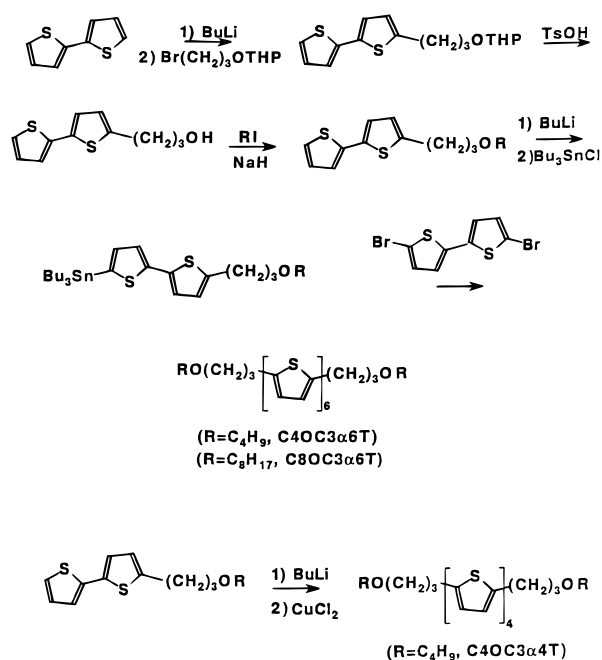
Scheme 1
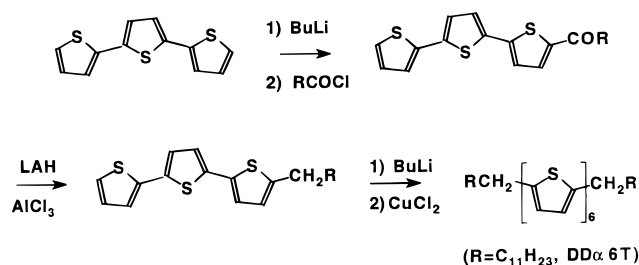
Scheme 2

Scheme 3

thus can be purified and converted to highly pure, less polar, monosubstituted half-oligomers. The monoalkyl oligomers are then coupled in the coventional way via lithio derivatives using $CuCl_2$ to form the target compounds. Dihexyl-α6T prepared in this manner has a high on/off ratio and was useful in defining the relative contributions of purity and morphology to device performance.[7] The effect of longer substituents than hexyl, or substituents containing heteroatoms in the chain, on the morphology, mobility, and liquid-phase-film-forming ability of thiophene oligomers has not yet been described.

In this paper, the synthesis, thin film morphologies, and field-effect mobilities of didodecyl- and dioctadecyl-α6T (DDα6T and DOα6T) are described, as well as those of two bis(3-alkoxypropyl)α6T derivatives (C8OC3α6T and C4OC3α6T) and one alkoxypropylated α4T (C4OC3α4T) (Schemes 2 and 3). This last compound was made in view of a recent report that α4T can more reliably approach longer oligomers in mobility if it is end-substituted.[13] Its synthesis was convenient since the α2T precursors were already available. The particular ether derivatives were chosen to optimize the thermal stability of the CO bonds (avoiding substitutable thienylmethyl or eliminatable thienylethyl ethers) and to produce the greatest enhancements in solubility while having the least deleterious effect on the molecular organization. All of the compounds were synthesized using variations of the polar intermediate strategy, with ketones as the intermediates leading to alkyl chains and tetrahydropyranyl (THP) ethers for the alkoxyalkyl substituents. Besides the $CuCl_2$ coupling, variations on the 2+2+2 Stille coupling described by Tour[14] and Wei[11] were particularly useful.

The synthetic methodology was also used to synthesize the previously reported DHα6T[6,7] and dihexyl-α4T

(DHα4T).[9] Mobilities of solution-cast films of these compounds were obtained and compared to those of the newly synthesized oligomers. In addition, DHα4T forms a vacuum-deposited film with a unique, single-crystal morphology that is described in detail in an accompanying communication.[15]

Experimental Section

Starting materials were purchased from Aldrich and used as received. Tetrahydrofuran (THF) was distilled from Na benzophenone ketyl. NMR spectra (proton) were collected on a Bruker 360 MHz spectrometer and referenced to tetramethylsilane. Thermal analyses were performed using a Perkin-Elmer DSC7 (differential scanning calorimetry) analyzer. Elemental analyses were done by Robertson Microlit Laboratories, Madison, NJ. Molecular modeling was performed using the Cerius system from Molecular Simulations, Inc.

TFTs were prepared as described elsewhere.[16] Briefly, thermally grown silicon dioxide dielectric was grown on n-doped silicon substrate "gates". For the typical "bottom contact" geometry, gold electrodes forming channels of 250 μm width (*W*) and 1.5−25 μm length (*L*) were photolithographically defined, and the semiconductor was deposited over the entire electrode/dielectric surface. For the occasional alternative "top contact" geometry, gold electrodes were defined after semiconductor deposition by using shadow masks with *W*/*L* of ca. 1.5 and device area of $(3-4) \times 10^{-2}$ mm². The electrical characterizations were performed at room temperature under vacuum using a 4145b Hewlett-Packard semiconductor parameter analyzer.

For morphological chracterizations, the materials were deposited onto carbon-coated electron microscope grids and Si/SiO₂ chips simultaneously with the TFTs. X-ray diffraction studies were done on the chips in the reflection mode at 40 kV and 250 mA. A 2 kW Rigaku X-ray generator was used as a source of Ni-filtered Cu Kα radiation. The films on the grids, used for electron microscopy, were shadowed with Pt/C at tan⁻¹

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0.5 and lightly carbon-coated in a vacuum evaporator before examination using a JEOL transmission microscope operated at 100 kV.

5-Dodecanoyl-2,2′,5′,2″-terthiophene. Terthiophene (4.0 g) was lithiated at −70 °C with BuLi (17.6 mmol, 1.1 equiv) in 150 mL of THF, transmetalated with 4.0 g (0.97 equiv) of MgBr$_2$ etherate, and condensed at 0 °C with freshly distilled dodecanoyl chloride (3.7 mL, 1 equiv) in 40 mL of THF using 1 mmol of Li$_2$MnCl$_4$ as a catalyst, as previously described for hexanoylterthiophene.[7] The purification sequence and yield (30%) were similar. NMR: 0.88 (CH$_3$), 1.3−1.8 (side chain), 2.86 (CH$_2$CO), 7.0−7.3 and 7.6 (ArH).

5-Dodecyl-2,2′,5′,2″-terthiophene. The above dodecanoyl compound (1 g as a solution in 20 mL of toluene) was reduced with excess LiAlH$_4$ (0.70 g) and AlCl$_3$ (0.61 g) in 150 mL of ether as previously described.[7] The yield after chromatography with hexane−silica gel was 75%. NMR: 0.88 (CH$_3$),1.3−1.4 (side chain), 1.68 and 2.79 (CH$_2$ CH$_2$CS), 6.68, 6.97−7.06, 7.15, 7.19 (ArH).

5,5′′′′′-Didodecyl-2,2′,5′,2″,5″,2‴,5‴,2⁗,5⁗,2′′′′′-sexithiophene. Dodecylterthiophene (0.75 g, 1.8 mmol) was lithiated with 1.1 equiv of BuLi and TMEDA in 70 mL of THF and then oxidatively dimerized with 0.48 g (2 equiv) of CuCl$_2$ as usual.[6,7] The product was recrystallized from mesitylene and vacuum sublimed. The yield after recrystallization was 0.23 g (31%). Anal. Calcd for C$_{48}$H$_{62}$S$_6$: C, 69.35; H, 7.52; S, 23.14. Found: C, 69.85; H, 7.27; S, 23.58.

Attempted Preparation of Dioctadecylsexithiophene. 5-Octadecylterthiophene was prepared by octadecanylation of lithiated terthiophene, with octadecyl iodide. However, the oxidative coupling reaction failed.

5-Octadecanoyl-2,2′-bithiophene. A mixture of 3.5 g of 2,2′-bithiophene and 9.5 g (0.85 equiv) of stearic anhydride was heated to the melt and then cooled until resolidification began. Boron trifluoride etherate (0.25 mL) was added with rapid swirling. The ensuing exotherm was moderated with a water bath. The temperature rose to 70 °C. Heat was then applied to melt all the solids, attaining a maximum temperature of 100 °C. Dioxane (100 mL) was added, the mixture was heated to reflux to dissolve the solids, 2 mL of water was added to decompose any unreacted anhydride, and the mixture was allowed to cool to room temperature to crystallize the product. The precipitated crystals were collected and washed with dioxane and ether and dried at vacuum. The yield was 6.7 g of purely monosubstituted solid bithiophene, with a 20% impurity of stearic acid. NMR: same as that for dodecanoylterthiophene except 7.03. 7.12, 7.29, and 7.58 for ArH.

5-Octadecyl-2,2′-bithiophene. The above product (6 g) was reduced with excess LiAlH$_4$ (3.4 g) and AlCl$_3$ (3.0) in 200 mL of ether as previously described except it was not necessary to add toluene and boil away the ether. The yield (unoptimized) was at least 40% after chromatography with hexane−silica gel. NMR: same as that for dodecylterthiophene except 6.62, 6.95, 7.08, 7.18 for ArH.

5-Octadecyl-5′-tributylstannyl-2,2′-bithiophene. The above product was dissolved in 150 mL of THF and treated with 1 equiv of BuLi at −70 °C. After the solution was warmed to 0 °C and recooled to −70 °C, 1 equiv (1.4 g) of Bu$_3$SnCl was added. After the solution was warmed to room temperature and partitioned between ether and aqueous NaCl, the product was isolated in >90% yield. NMR: 6.63, 6.96, 7.02, 7.19 (4 d, ArH).

5,5′′′′′-Dioctadecyl-2,2′,5′,2″,5″,2‴,5‴,2⁗,5⁗,2′′′′′-sexithiophene. A solution of 1.6 g of the above product, 0.33 g of 5,5′-dibromo-2,2′-bithiophene,[17] and 60 mL of Pd(PPh$_3$)$_4$ in 30 mL of toluene was stirred for 2 h at room temperature and then for 20 h just below reflux. The red precipitate was collected from the hot solution and washed with 2 N HCl, water, and acetone to yield 0.7 g of crude product. Recrystallization from 75 mL of mesitylene with hot filtering gave 0.31 g (35%) of purified product. Material for analysis and TFT

fabrication was further refined by sublimation. Anal. Calcd for C$_{60}$H$_{86}$S$_6$: C, 72.09; H, 8.67; S, 19.29. Found: C, 71.67; H, 8.52; S, 19.76.

5,5′′′′′-Dihexyl-2,2′,5′,2″,5″,2‴,5‴,2⁗,5⁗,2′′′′′-sexithiophene. The same reaction sequence was used as for the dioctadecyl compound, starting with 6.2 g of bithiophene and 8.0 g of hexanoic anhydride, to obtain the sample used for the liquid-phase deposition experiment. The hexanoylbithiophene precursor (mp 64−66 °C) was dissolved in toluene, washed cautiously with NaHCO$_3$, dried, filtered, concentrated, and chromatographed before reduction with LiAlH$_4$/AlCl$_3$ on the same scale as for the octadecanoyl case. The NMR spectra were identical with those of the octadecyl derivatives except for the intensities of the methylene signals.

5,5‴-Dihexyl-2,2′,5′,2″,5″,2‴-quaterthiophene. The standard BuLi/CuCl$_2$ coupling was performed on 2.4 g of the hexylbithiophene prepared as described above. A standard aqueous/organic workup was performed, quenching with dilute HCl and adding toluene to the organic layer. The concentrated organic reaction mixture was triturated with hexane and methanol to obtain solid product, pure by NMR. The yield was 58% based on consumed starting material (not accounting for lithiate quenched by adventitious water or HCl). Mp: 183 °C. Anal. Calcd for C$_{28}$H$_{34}$S$_4$: C, 67.42; H, 6.87; S, 25.71. Found: C, 67.29; H, 6.89; S, 25.91.

5-(3-Tetrahydropyran-2-yloxypropyl)-2,2′-bithiophene. Bithiophene (3.7 g) was lithiated with 1 equiv of BuLi at −70 °C as usual in 100 mL of THF and alkylated with 1 equiv (5.0 g) of 2-(3-bromopropoxy)tetrahydropyran at room temperature overnight. Quenching with dilute hydrochloric acid under N$_2$ and partitioning between ether and water gave a crude product with an unexplained blue color. Chromatography with hexane/CH$_2$Cl$_2$ on 80 g of silica gel gave purified product (3.7 g) as an oil in 50% yield, but the blue color persisted. NMR: 1.5, 1.65, 1.8, 1.95 (methylenes), 2.90 (CH$_2$-CS), 3.45 and 3.85 (CH$_2$ O), 4.56 (methine), 6.70, 6.99, 7.08, 7.17 (ArH).

5-(3-Hydroxypropyl)-2,2′-bithiophene. The above product (5.0 g) was deprotected with 0.5 g of toluenesulfonic acid in 100 mL of methanol at reflux for 30 min. Partitioning between ether and aqueous NaHCO$_3$ gave 2.6 g of pure solid product (72% yield). NMR: 1.3 (OH), 1.92, 2.89, 3.69 (methylenes), ArH as for the THP derivative.

5-(3-Butoxypropyl)-2,2′-bithiophene and 5-(3-Octyloxypropyl)-2,2′-bithiophene. The hydroxypropyl product above was alkylated with either butyl iodide or octyl iodide using NaH as base and 20 mL of refluxing dioxane per gram of starting material as solvent. About 3.5 equiv of iodide and base were needed for reasonable conversions. The reaction mixtures were filtered, concentrated, and chromatographed on silica gel with hexane−CH$_2$Cl$_2$ elution to give product in >50% yield. NMR: 0.88 (methyl), 1.3−1.4 (internal methylene), 1.56, 1.94, 3.3, 3.4 (methylene), ArH as for the THP derivative.

These products were stannylated (NMR: side chains as for the nonstannylated derivatives, ArH as for the octadecyl stannyl bithiophene) and converted to their respective α6T derivatives as described for the octadecyl compound. The butoxy derivative was also dimerized to the α4T derivative (NMR: 0.88, 1.3−1.4, 1.95, 3.4−3.5 (side chain), 6.69, 7.0, 7.05 (ArH)) as described for dihexyl-α4T. The crude α6T solids were collected at room temperature rather than from the hot reaction solutions. The yields of recrystallized product were >40%. Analytical samples were sublimed prior to use.

5,5′′′′′-Bis(3-butoxypropyl)-2,2′,5′,2″,5″,2‴,5‴,2⁗,5⁗,2′′′′′-sexithiophene. Anal. Calcd for C$_{38}$H$_{42}$O$_2$S$_6$: C, 63.12; H, 5.85; S, 26.60. Found: C, 62.96; H, 5.74; S, 26.57.

5,5′′′′′-Bis(3-octyloxypropyl)-2,2′,5′,2″,5″,2‴,5‴,2⁗,5⁗,2′′′′′-sexithiophene. Anal. Calcd for C$_{46}$H$_{58}$O$_2$S$_6$: C, 66.24; H, 6.95; S, 23.06. Found: C, 65.94; H, 6.88; S, 23.04.

5,5‴-Bis(3-butoxypropyl)-2,2′,5′,2″,5″,2‴-quaterthiophene. Anal. Calcd for C$_{30}$H$_{38}$O$_2$S$_4$: C, 64.47; H, 6.85; S, 22.96. Found: C, 64.41; H, 6.78; S, 22.93.

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Results and Discussion

Didodecyl-α6T was synthesized using the sequence that we had previously outlined for the dihexyl compound, shown in Scheme 1. The dioctadecyl derivative could not be synthesized the same way because of the resistance of octadecylterthiophene to dimerization by the lithiation/oxidative coupling method. We were therefore motivated to seek an alternate synthesis that still enabled convenient isolation of a monofunctionalized precursor. The acylation of thiophene by acetic anhydride has long been known,[18] and the bithiophene acylation described here is a modification of that reaction. The thienyl ketone products are easily isolated by crystallization or chromatography and utilized as illustrated in Scheme 2. The ensuing reduction is similar to one we previously described, and the Stille coupling sequence is based on very recent literature precedents.[11,14] The ketones and alkylthiophenes are easily distinguished by their NMR spectra, with downfield-shifted protons on both the ring (7.6 ppm) and chain (2.9 ppm) carbons adjacent to the carbonyls. This sequence is undoubtedly generalizable to many end-substituted thiophene oligomers whose substituents can arise from available anhydrides, and we now consider this method to be more reliable than the ones based on lithiation and oxidative coupling. The Stille coupling could also be used to synthesize quaterthiophenes, particularly unsymmetrical ones, from mixtures of stannylated and brominated bithiophenes, but since the quaterthiophenes used here were symmetrical, the oxidative coupling with $CuCl_2$ saved the bromination step.

The synthesis of the ether-substituted oligomers is shown in Scheme 3. Again, the general idea of proceeding through an acetal precursor should be widely applicable, although here the sequence is particularly convenient because of the commercial availability of the THP-protected bromo alcohol. The alkylation step would probably be even more efficient with a protected iodo alcohol. The methylenes α to the acetal (3.5 and 3.8 ppm) and the acetal methine (4.6 ppm) are characteristic proton NMR signals for the intermediates.

The thermal behavior of the compounds was determined by a repeated heating–cooling cycle using the DSC. All of the alkylated α6T and α4T compounds have reversible melting peaks and mesophases as illustrated in Figure 1. Generally, the melting points decrease as (a) the alkyl chains are lengthened as in the case of DDα6T and DOα6T and (b) as the number of thiophene rings are decreased, i.e., α6T compounds vs α4T compounds. Insertion of an O atom in the alkyl chains as for the case of butylpropoxy α6T and α4T tends to slightly decrease the melting point. The reversibility of the melting peaks is maintained for C4OC3α4T but is not observed for the corresponding α6T. The oxygenated compounds show no obvious mesophases.

Sublimed films of all of the α6T and α4T compounds described in this paper display an edge-on orientation, as already documented.[19] The repeat spacing perpendicular to the substrate, listed along with the TFT mobilities in Table 1, is in good agreement with a
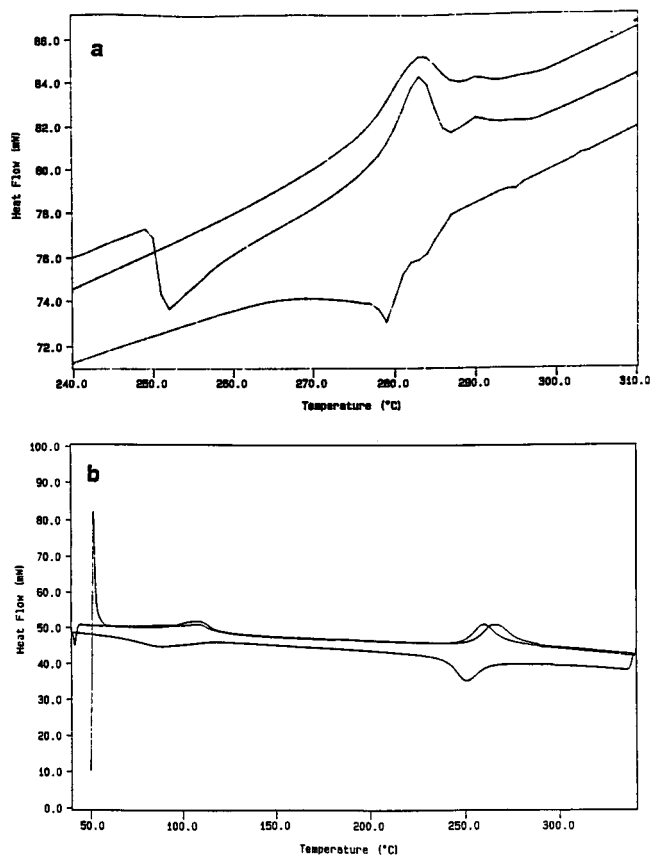
Figure 1. DSC scans of (a) DDα6T and (b) DOα6T under a N_2 atmosphere. The feature at 250 °C in (a) is an artifact.

Table 1. Properties of Sublimed Oligomer Films on Si/SiO₂

| compound	mp, °C	repeat spacing, Å	resolution	mobility, cm²/Vs
DHα6T	>300	36[6]	excellent	0.04[6,7]
DDα6T	282	48	very good	0.016
DOα6T	268	ca. 70	poor (shoulder on main beam)	0.0013
C4OC3α6T	292	35	excellent	0.033[a]
C8OC3α6T	272	55	good	0.009[b]
C4OC3α4T	168	30	fair	0.004–0.008 0.003[a]
C4OC3α4T[c]		32	good	0.0009

[a] top contact, [b] annealed 125 °C, 5 s, [c] 80 °C substrate temperature during deposition

molecular length calculated on the basis of an extended conformation with the alkyl chains projected nearly perpendicular to the substrate and the conjugated cores bent at an angle. For DOα6T, a shoulder was seen overwhelmed under the main beam at ca. 1.3° 2θ. The morphologies are generally smooth or well-interconnected microcrystalline with 20–50 nm crystallite size, favorable for good TFT behavior. Exceptions to this general observation are DOα6T, where some of the grains are elongated, and C4OC3α4T deposited at 80 °C, where the domains take the form of micrometer-sized plates with spaces as large as 100 nm between them, a less favorable morphology for TFTs (Figure 2).

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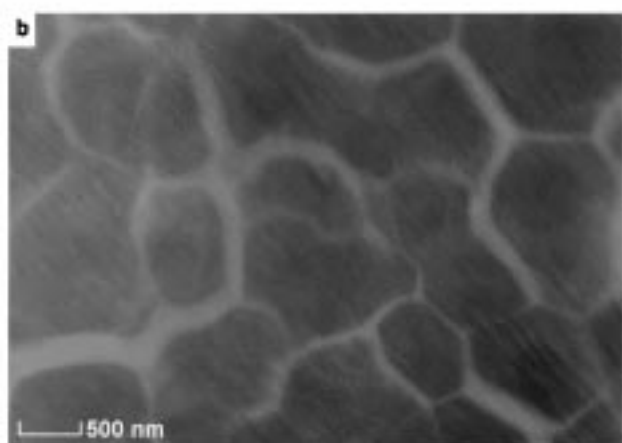
Figure 2. Transmission electron micrographs of (a) DOα6T films deposited at room temperature and (b) C4OC3α4T deposited at 80 °C.
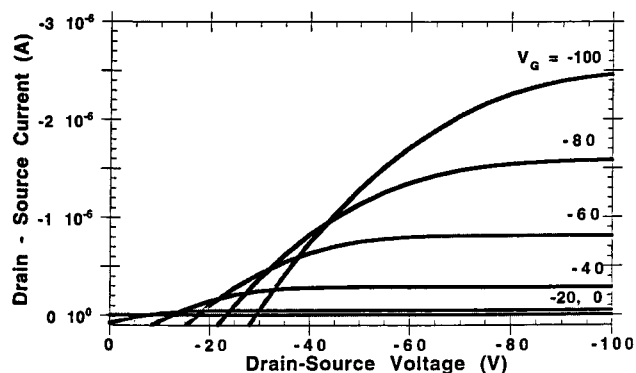
Figure 3. Electrical characteristics of sublimed C4OC3α6T films (top contact geometry) deposited at 100 °C. The increasingly negative *x*-intercepts with increased gate voltage are due to leakage through the dielectric.

The presence of oxygen in the side chain has little effect on the intermolecular packing or the apparent molecular length; the ether oxygen seems essentially isostructural with the methylene groups.

The TFT mobilities of sublimed films of the new α6Ts, except for DOα6T, are at the low end of the 10^{-2} cm²/Vs range, typical for such compounds other than the dihexyl version.[6,7] An example is shown in Figure 3. The mobility seems to decrease with chain length, depending little on whether the chain contains an
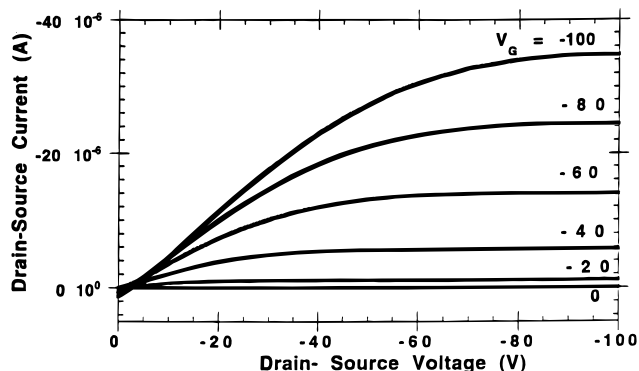
Figure 4. Electrical characteristics of cast DHα6T films (bottom contact geometry). Solvent was evaporated in a vacuum oven at 100 °C. The on/off ratio is >10000.

oxygen, with the most disordered and longest molecule, dioctadecyl-α6T, displaying the lowest mobility, close to 10^{-3} cm²/Vs. We cannot rule out contact difficulties as a factor in the low apparent mobility of this compound; if its film presents an alkane-like skin to the metal electrodes, a substantial series resistance could result. Still, the mobility is substantial considering that over half of the molecular volume consists of insulating hydrocarbon chains. The mobility of the α4T diether derivative is unremarkable for an α4T, and its morphology is not especially well ordered. However, the behavior of DHα4T is surprisingly different, with much higher mobility and crystallinity, and is described in detail in a separate, accompanying communication.[15]

As was previously suggested,[11] the presence of an oxygen in the side chain does increase the solubility of dialkyl α6Ts, with C4OC3α6T about twice as soluble in aromatic solvents as DHα6T. The effect is observed with only minimal heteroatom substitution and is diminished as the chain becomes long enough to contribute additional packing forces. The slight increase in rotational freedom of an internal ether group and the weak polar interaction with solvents are probably responsible for this solubility change. It is possible that a more elaborate polyether side chain, such as methoxypropoxypropyl, might confer some additional solubility, but at the expense of further synthetic manipulation and hydroscopicity. As discussed below, the oxygen atom appears to diminish the mobility, and presumably the ordering, of solution-cast films relative to the all-methylene-chain-substituted thiophene oligomer films.

Solutions of oligothiophenes for liquid-phase deposition on TFTs were on the order of 0.1% in chlorobenzene or 1,2,4-trichlorobenzene, prepared by simply heating the solids and liquids together in centrifuge tubes. For these experiments, bottom contact substrates were used. Solutions were applied dropwise onto the substrates, and for films cast from chlorobenzene, the solvents were evaporated from the devices in a vacuum oven at three different oven temperatures, room temperature, 70 °C, and 100 °C. Films cast from trichlorobenzene were only dried at 70 °C. No attempt was made to further optimize the deposition conditions, and as a result, the films were not of uniform thickness, leading to varied morphologies and mobilities among devices on a single substrate.

Nevertheless, order of magnitude determinations of the mobilities were made for four compounds, listed in

Table 2. Mobilities of Oligomer Films Cast from Solution[a]

compound	CB, RT	CB, 70 °C	CB, 100 °C	TCB, 70 °C
DHα6T		$(0.4-1) \times 10^{-2}$	$(0.5-3.5) \times 10^{-2}$	$(1.5-5) \times 10^{-2}$
C4OC3α6T	$(1-4) \times 10^{-3}$	$(0.6-1) \times 10^{-2}$	$(0.2-1) \times 10^{-2}$	$(0.5-1) \times 10^{-2}$
DHα4T		$(1-9) \times 10^{-3}$	$1.5 \times 10^{-3}-0.07$	$(0.3-1) \times 10^{-2}$
C4OC3α4T	$(4-7) \times 10^{-4}$	$(0.6-1) \times 10^{-3}$		$(0.5-4) \times 10^{-4}$

[a] CB = chlorobenzene solvent. RT = room temperature. TCB = 1,2,4-tricholorobenzene solvent. Temperatures are during solvent evaporation. Units are cm²/Vs.

Table 2. The highest mobilities were obtained with DHα6T, *approaching those that have been reported for evaporated films of this compound*.[6,7] The characteristics for this sample are shown in Figure 4. The oxygenated α6T had a slightly lower mobility under comparable deposition conditions, as did DHα4T, but the latter compound showed greater inconsistency, and its mobility is not as well defined and may be higher than we have definitively observed. Perhaps the oxygen substitution and the oligomer shortening, both of which enhance solubility, also lessen the tendency toward ideal packing as the solvent is removed. The oxygenated α4T, with both of these influences, had the worst TFT performance, and no meaningful temperature dependence could be obtained therefrom. Data for C4OC3α6T indicate that the elevated drying temperature is advantageous, while only DHα6T displayed a significant solvent dependence. It may be expected that an extensive survey of side chains, solvents, dielectric surfaces, and drying conditions would uncover a procedure for improved performance and reproducibility in solution-cast TFTs.

Conclusion

New methods for the synthesis of various α,ω-disubstituted oligothiophenes have been developed, and their thermal, morphological, and hole-transporting properties assessed. The incorporation of an oxygen atom in the side chain was shown to have no effect on the repeat spacing and packing of the solid films, and only a minor negative effect on the mobility of a substituted α6T, accompanied by an increase in the solubility. There was a deleterious effect of a side chain oxygen on the properties of a substituted α4T. TFTs with significant mobilities were fabricated by simple deposition of dilute oligomer solutions onto electrode-patterned substrates. Preparation of the semiconductor material in the liquid-phase-deposited devices did not require conversion of a precursor or other postdeposition chemistry. This work thus represents an advance toward the fabrication of all-liquid-phase-processed electronic devices, with future efforts being aimed at the selective application of semiconductor solutions to defined regions of substrates and to the surfaces of polymer dielectrics.