ducible pressure vs area isotherms. The apparent cross-sectional area (<20 Å^2/molecule) at high film pressure for C_{60} suggests that on compression the films become multilayered. However, we were unable to produce a film of pure C_{60} that remained as a monolayer at pressures above 65 mN/m; our films collapsed at pressures of 32–36 mN/m. Nor were we able to produce a monolayer having a molecular area near 90 Å^2 by spreading from a dilute solution.

In conclusion, we have shown that $C_{60}/C_{18}OH$ mixtures give reproducible pressure vs area isotherms with small apparent areas per molecule. We have successfully transferred the mixture to fused silica by the L–B technique as an ultrathin film which can be used for further study.

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Registry No. C_{60}, 99685-96-8; $C_{18}OH$, 112-92-5.

Electrooxidation of Soluble α,α-Coupled Thiophene Oligomers

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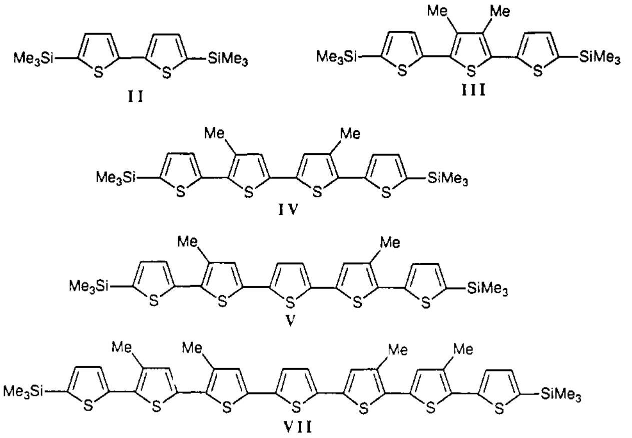
The electrooxidation reactions of polythiophene films produce complicated cyclic voltammograms. The waves are often broad and deformed and appear at the foot of a large anodic current which often continues to rise until the films are decomposed or "burned" off of the electrode.[1-10] There is often a prewave as a shoulder,[4-10] and its visibility varies with the film thickness, substituents on the polymer,[5-7] and electrolyte.[4,8] A recent electrochemical ESR study showed that the prewave is associated with the one-electron oxidation to produce the polaron state and the main peak corresponds to the formation of bipolarons.[4] In contrast, the electrochemical oxidation of the thiophene dimer, trimer, tetramer, and hexamer in liquid SO_2 at −44 °C, in CH_3CN and in nitrobenzene leads to well-separated anodic processes.[11-13] The electrochemistry of the higher oligomers has not been reported even though there are many recent studies on the chemistry of these compounds.[13-20] In this study, α,α-coupled thiophene oligomers with terminal α-$(CH_3)_3Si$ groups (α-TMS) and β-CH_3 groups are used to study the importance of the second oxidation reaction at room temperature as a model study for the polymer segments in the absence of irregular couplings,[21] molecular weight distributions,[22] lattice interactions,[23] capacitance,[24,25] and resistance[26] as may occur in a film.

Table I. Summary of Electrochemical Data

oligomer	E_{pa_1}, E_{pa_2}, V	ΔE_p, mV	n_1, $n_1 + n_2$	$E(h\nu)$, eV
VII	0.86, 1.04	60, 80	1.06, 2.05	2.36
V	0.98, 1.20	60, 70	1.04, 1.98	2.52
IV	1.04, 1.36	70, 100		2.68
III	1.16, 1.53	80	0.95	3.04
II	1.46[a]			3.43

[a] Reported E_{pa} values for II and bithiophene are 1.14 and 1.32 V in CH_3CN, respectively.[30]

Chart I



The soluble α,α-coupled thiophene oligomers with the terminal α-TMS groups and β-methyl groups were prepared by Ni- and Pd-catalyzed reactions of the corresponding halide, stannane, or Grignard derivatives.[27] The cyclic voltammetry and chronocoulometry of the oligomers (10^{-4} M) in 0.1 M $Bu_4N\ BF_4/CH_2Cl_2$ solutions were recorded using a 0.5-cm Pt electrode and an SCE double junction electrode and with a PAR Model 273. The electrochemical data are summarized in Table I. The heptamer VII (Chart I), pentamer V, and tetramer IV all show two one-electron redox waves which can be cycled

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with chemical reversibility. The peak separations for the second oxidation is slightly higher (70–100 mV) but similar to the separation observed with FeCp$_2$ (E_{pa} = 0.59 V, ΔE = 70 mV). The i_{pa} values scale linearly with the square root of the sweep rate as expected for a diffusion-limited reaction. Chronocoulometry for the first reaction showed a linear q vs $t^{1/2}$ dependence. For VII, D is 1.2×10^{-5} cm^2/s, and n is 1.04 for the first oxidation, where n is obtained from a comparison of $nD^{1/2}$ from the slope in the q vs $t^{1/2}$ plot with $n^{3/2}D^{1/2}$ from the slope in the i_{pa} vs $\nu^{1/2}$ plot. With this same procedure, n equal to 0.99 was obtained with ferrocene. For the second oxidation, n equal to ca. 1 was obtained from the relative slopes in the q vs $t^{1/2}$ plots for steps anodic of the first and the second wave, respectively. Similar values were obtained for V. The ca. 0.2-V separation between the two waves parallels the separation observed with unsubstituted polythiophene films[4] and those containing alkoxy[5,6] and methyl[8-10] groups. The second oxidation is irreversible with the timer III and not visible with the dimer II. Thus four or more thiophene units are required to stabilize the dication at room temperature.

The E_{pa} values for the five oligomers in Table I plot linearly with both 1/(the number of rings) with slope 1.7 and with the band edge in the visible spectrum of the neutral oligomer with slope 0.57. The corresponding slopes for the unsubstituted series are 1.5 and 0.52, respectively.[28] Thus in solution, the methyl groups do not affect the π-conjugation in the monotonically increasing segments as is observed with other substituents,[29] and the α-TMS group is known to have a small effect on the redox potential.[30] The VII and V dications support 0.3–0.4 charges/ring, which compares well with the stable oxidation level (average) of 0.06–0.35 charges/ring for polythiophene films.[1,2,8,31-36]

Chemical oxidation[13,17,18] of V and VII with 2 mol of FeCl$_3$ yields the radical cation as evident by the strong signal in the ESR spectrum with $g = 2.004$ which almost vanishes upon further oxidation with an additional 2 mol of FeCl$_3$. Therefore, the two oxidation waves observed electrochemically correspond to the successive formation of the radical cation and dication. Concurrent with the evolution of the ESR signal is a dramatic change in the vis/near-IR spectra. The absorption at 447 nm for the neutral VII disappears upon oxidation to the radical cation and double peaks appear at 745 and 829 nm and at 1427 and 1785 nm (blue) in line with previous reports.[13,17,18] The radical cation is stable at room temperature for at least several hours. Further oxidation to the dication changes the absorption spectrum, and only peaks at 1064 and 1230 nm are observed. Similar changes are observed in the spectra for the pentamer except that the absorptions are blue shifted. Finally, III can be oxidized to the radical cation which has a strong ESR signal ($g = 2.004$) and shows two major peaks at 557 and 878 nm in the vis/near-IR spectrum.

In summary, the stepwise oxidation to form the stable radical cation and dication can be accomplished at room temperature with thiophene oligomers containing four or more units. The ca. 0.2-V separation between the first and second oxidation suggests that two separate oxidation waves should be visible in the room-temperature voltammogram for the next higher oligomers and for the π-conjugated segments of polythiophene. This is in marked contrast with the conclusion that conducting polymers are expected to be oxidized in one broad single step.[11,37-39] The broad, featureless voltammograms observed with the polythiophene films may not be an inherent property of the polymer segments but instead may reflect the complications caused by irregular couplings,[21] molecular weight distributions,[22] lattice interactions,[23] film capacitance,[24,25] and resistance.[26]

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Registry No. II, 127729-23-1; III, 138983-70-7; IV, 138983-73-0; V, 138983-74-1; VII, 138983-79-6.

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Condensed Aryl-Bridged Siliconates. New Ladder and Network Ionomers

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Siliconates have been implicated as intermediates in many nucleophilic substitution reactions at silicon.[1-8] Coordination to silicon by electron-withdrawing (fluoride) and chelating (catechol) groups can result in the formation of *stable* five- and six-coordinate siliconates. Structural data for these complexes have been reviewed.[9] It is in-

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