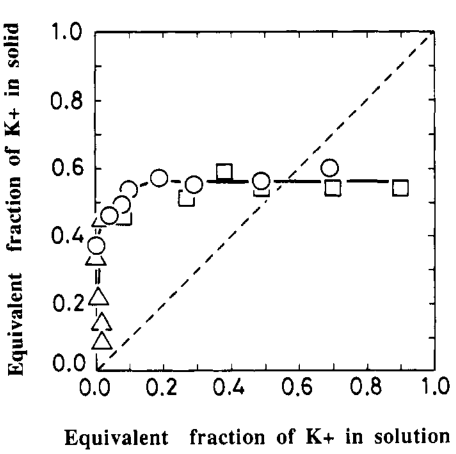

Figure 2. $Na^+ \rightleftharpoons K^+$ exchange isotherms on NaT at constant total molarities of 1.0×10^{-2} (○), 2.5×10^{-3} (△), and 2.5×10^{-2} M (□).

Table I. K^+ Ion Selectivity (K^+ Uptake, ppm) on NaT (1 g) in 40 cm^3 of NaCl + KCl Solutions with an Excess of Na^+ Ions

	initial K^+ concn, ppm			
Na^+/K^+	200	300	400	500
10	110.8	120.7	112.3	125.9
20	112.2	120.7	114.8	123.2
30	112.2	110.0	120.5	124.1

the low-concentration region of K^+ ions. The superior preference for K^+ ions over Na^+ ions on NaT was found to be independent on the total molarity as is shown in Figure 2. The characteristics for the selective K^+ ion uptake of NaT were further examined in the presence of a large excess of Na^+ ions. From the results, NaT was found to selectively take up a regular amount of K^+ ions without depending on the concentrations of Na^+ and K^+ ions as is seen in Table I.

In conclusion, these basic studies suggest that NaT can be utilized in the separation and immobilization of K^+ ions from the system which has a large quantity of Na^+ ions and a small quantity of K^+ ions, for example, seawater (Na^+, 10 500 ppm; and K^+, 380 ppm). The relation between the selectivity and structural change on fluormicas will be discussed in detail in a following paper.

Potential Dependence of the Conductivity of Polyacetylene: Finite Potential Windows of High Conductivity

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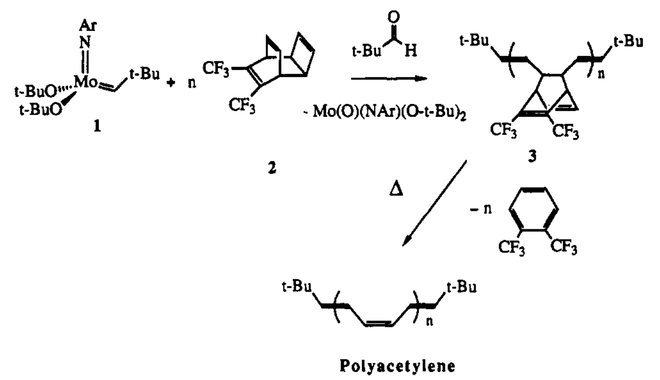
We wish to communicate that polyacetylene, the "prototypic" conducting polymer, exhibits a finite potential window of high conductivity upon oxidation in liquid SO_2 or upon reduction in tetrahydrofuran. These findings are analogous to those obtained for other conjugated polymers (polyaniline,[1] polythiophenes,[2,3] and polypyrroles[2]) and establish that a finite potential window is a general feature of conductivity in such polymers. The observation of finite potential windows of high conductivity in conjugated polymers is in accord with theoretical studies[4-6] that indicate it should be possible to oxidize or reduce them sufficiently to render them nonconducting.

Scheme I



Polyacetylene samples were prepared via a controlled version[7] of the Durham route,[8] as shown in Scheme I.[9] Samples of **3** were prepared by using a 60:1 ratio of monomer to catalyst; polydispersities were ≤1.18.[10] Films of **3** were cast onto arrays of individually addressable platinum macro- and microelectrodes[11] having a total area of ~0.04 cm^2, and the arrays were heated to 120 °C for 3 min to generate the polyacetylene films. Two individually addressable electrodes connected by a redox active polymer can be operated in a transistor-like configuration to reveal the potential dependence of the conductivity of the polymer. When a small fixed-potential difference (drain voltage V_D) is applied between the two electrodes, the magnitude of the current, I_D, between the electrodes is directly proportional to the conductivity of the polymer, which changes as the electrochemical potential (V_G) is changed. Therefore, a plot of I_D vs V_G gives relative conductivity vs potential.[12]

Figure 1a shows the cyclic voltammogram for a polyacetylene film in liquid SO_2/0.1 M $[(n\text{-}Bu)_4N]AsF_6$ at −70 °C. At potentials negative of ~0.7 V vs poly(vinyl-

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[11] The platinum arrays will be described fully in a future publication. For the purposes of the I_D–V_G, current passes between two platinum electrodes, ~0.1 μm high, ~1.5 mm long, ~1.2 mm wide, and separated from each other by ~35 μm. Four microelectrodes, ~1.5 mm long × ~4 μm wide, which lie between the two larger electrodes, are used for four-point probe measurements when the polymer is maximally conducting.

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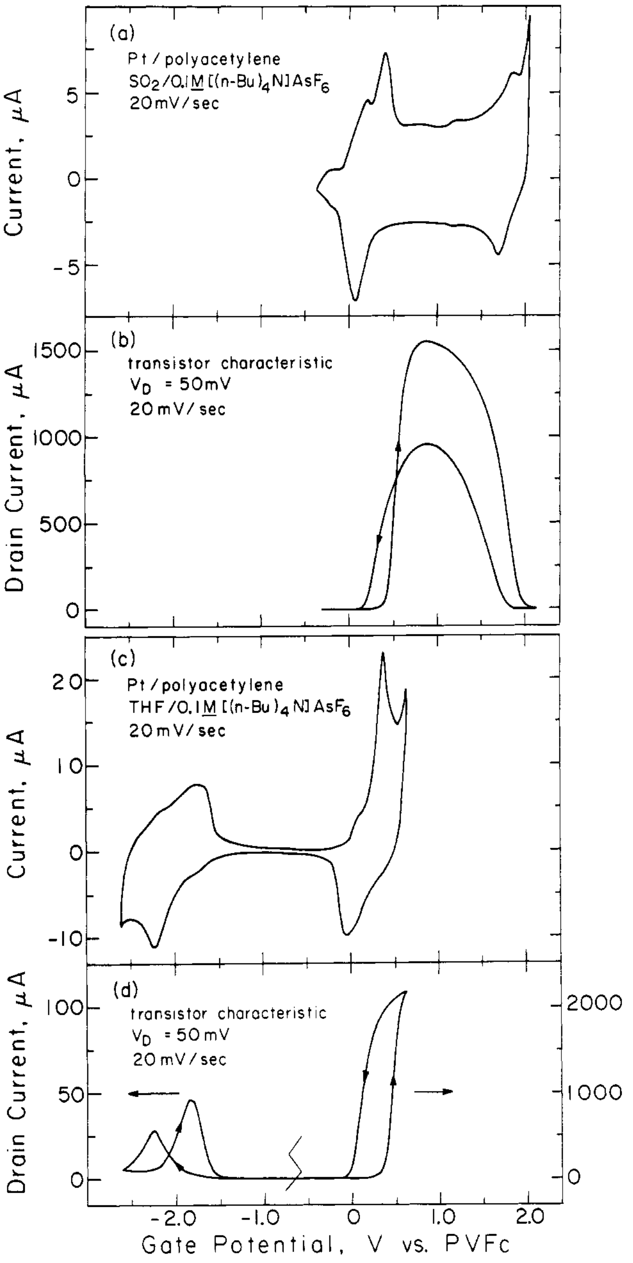

Figure 1. (a) Cyclic voltammetry of a polyacetylene film (containing 6×10^{-9} mol of double bonds) on a platinum electrode array in SO_2/0.1 M $[(n\text{-Bu})_4N]AsF_6$ at -70 °C. (b) I_D–V_G characteristic in SO_2/0.1 M $[(n\text{-Bu})_4N]AsF_6$ for the polyacetylene film characterized in (a). (c) Cyclic voltammetry of a polyacetylene film (containing 3×10^{-8} mol of double bonds) on a platinum electrode array in tetrahydrofuran/0.1 M $[(n\text{-Bu})_4N]AsF_6$ at room temperature. (d) I_D–V_G characteristic in tetrahydrofuran/0.1 M $[(n\text{-Bu})_4N]AsF_6$ for the polyacetylene film characterized in (c). The drain current scale on the right corresponds to the region in which polyacetylene is oxidized, and the scale on the left corresponds to the region in which polyacetylene is reduced.

ferrocene) (PVFc)[13,14] the features of the voltammogram correspond to those previously reported in other solvent/electrolyte systems.[15] In a previous study of polyacetylene in liquid SO_2/electrolyte,[16] the polymer was found to be more durable than in propylene carbonate, but it was not oxidized to as high a level as we report, nor was its conductivity measured. In the region of more positive potential, we observe new features, anodic and cathodic peaks at ~1.8 and ~1.6 V vs PVFc, respectively. Figure 1b shows the I_D–V_G characteristic for two platinum electrodes connected by a polyacetylene film in liquid SO_2/0.1 M $[(n\text{-Bu})_4N]AsF_6$. The increase in I_D, coinciding with the initial oxidation peak in the cyclic voltammogram, indicates a sharp rise in conductivity. I_D reaches a maximum at ~0.8 V and then declines dramatically upon further oxidation, thereby defining a finite potential window of high conductivity. Hysteresis in the I_D–V_G curve is independent of scan rate and correlates with peak splitting in the cyclic voltammogram. The same behavior is observed for other conducting polymers[2] and has been explained in terms of potential-dependent changes in polymer structure.[17] The difference between magnitudes of I_D on the positive and negative potential sweeps is not due to degradation of the polymer, as the curve is retraced on subsequent scans. The maximum conductivity on the positive sweep (occurring at ~0.8 V) is ~20 Ω^{-1} cm^{-1}, in agreement with conductivities reported for unoriented Durham polyacetylene.[18] The width of the region in which conductivity is at least 10% of the maximum is 1.36 V. Of the conducting polymers, polyacetylene has the highest conductivities (up to ~10^5 Ω^{-1} cm^{-1}) to have been reported[19] and also has the widest window of high conductivity to have been measured. For comparison, the widths of the windows for poly(3-methylthiophene) and for polyaniline are ~1.08 and ~0.54 V, respectively.[2]

For electrodes onto which different quantities of precursor polymer have been cast, the integral of the cyclic voltammogram scales linearly with the amount of polymer cast, indicating that all the polyacetylene is in electrical contact with the array. Integration of the cyclic voltammogram in Figure 1a indicates that at 0.8 V, polyacetylene is oxidized to the extent of ~0.1 electron/double bond. This value agrees with theoretical predictions for the extent of oxidation at which maximum conductivity occurs.[6] In previous electrochemical studies carried out in other solvent/electrolyte systems, it was found that oxidation beyond these levels led to irreversible loss of electroactivity and conductivity.[20] In liquid SO_2/electrolyte, however, it is possible to oxidize polyacetylene to a much greater extent without chemical degradation; at the positive potential limit shown in Figure 1a, the polymer is oxidized to the extent of ~0.2 electron/double bond, indicating that the highest occupied electronic band remains significantly populated.[2] It is noteworthy that conductivity at this

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potential ($\sim 10^{-2}\ \Omega^{-1}\ \text{cm}^{-1}$) is still much greater than that of the neutral film ($<10^{-6}\ \Omega^{-1}\ \text{cm}^{-1}$).

Parts of c and d of Figure 1 show the cyclic voltammogram and the I_D–V_G characteristic, respectively, of polyacetylene in tetrahydrofuran/0.1 M $[(n\text{-Bu})_4\text{N}]\text{AsF}_6$. The I_D–V_G curve shows that polyacetylene also has a finite potential window of high conductivity (~0.9 V wide) when it is reduced. A maximum in conductivity as a function of potential for electrochemically reduced polyacetylene has been reported previously.[21] Integration of the voltammogram in Figure 1c indicates that at the potential of maximum conductivity, polyacetylene is reduced to the extent of ~0.05 electron/double bond, while at the negative potential limit shown, the polymer is reduced by ~0.1 electron/double bond. Figure 1d shows a ~100-fold difference in conductivity for the reduced and oxidized polyacetylene film. A similar finding has been reported for reduced vs oxidized polythiophenes.[3] The conductivity of reduced polyacetylene has been reported to be quite sensitive to the size of the intercalating cation.[22] However, we obtain similar conductivities using either $[(n\text{-Bu})_4\text{N}]\text{AsF}_6$ or NaAsF_6 as the electrolyte. Unoriented Durham polyacetylene has been reported to be substantially less crystalline than polyacetylene prepared by other methods,[17] and this may explain why the maximum conductivity does not show a cation dependence. The highest conductivities reported to date for oxidized polyacetylene[19] are significantly larger than any high conductivities reported for reduced polyacetylene;[23] however, this is the first time that conductivities of oxidized and reduced polyacetylene have been compared in a single experiment on the same sample. These results establish that the intrinsic conductivity of reduced polyacetylene is significantly lower than that of oxidized polyacetylene, as is indicated by published data.[19,21,23,24] They are also in agreement with calculations predicting higher conductivity for polyacetylene when it is oxidized than when it is reduced,[25] which, in turn, are based on calculations that anions are more localized on polyacetylene chains than are cations.[5]

The observation of a finite potential window of high conductivity for polyacetylene is consistent with theoretical expectations and establishes that this effect is general for conducting polymers. It appears that polyacetylene, the most highly conducting of these polymers, also has the widest potential window of high conductivity upon oxidation and that it is more conducting when oxidized than when reduced. We are currently making use of our ability to synthesize highly monodisperse polyacetylene and polyene oligomers[8,9] in order to study the dependence of conductivity upon chain length.

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Molecular Control of Surface Film Compositions via Pulsed Radio-Frequency Plasma Deposition of Perfluoropropylene Oxide

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Surface modifications employing plasma polymerizations represent a very active research area at the present time.[1] Examples of improved surface properties obtained via this approach have been demonstrated with materials employed in biocompatibility studies,[2] inert coatings to reduce oxidative degradation,[3] and membrane permselectivity[4] to mention but a few of the many applications under current development. To date, the overwhelming majority of these plasma polymerization studies have been carried out using continuous wave (CW) systems with an emphasis on adjusting plasma variables (e.g., reactant pressure and flow rate, absorbed radio-frequency (rf) power) to produce uniform films on targeted substrates.

The purpose of the present communication is to illustrate that the use of a pulsed rf plasma, in lieu of the CW mode, can provide an important added dimension in plasma-induced surface modifications. Specifically, we wish to report a level of control over the molecular composition of the surface modifications achieved as a function of the rf duty cycle employed. This surface modification controllability is demonstrated in the present case by the pulsed rf plasma deposition of hexafluoropropylene oxide (C_3F_6O) in which marked changes in film composition are noted as a function of the rf duty cycles employed. The variation in molecular composition of the surface depositions is established by both XPS and FT-IR analyses of the resultant films.

The pulsed rf plasma polymerizations were carried out in a cylindrical Pyrex glass reactor 10 cm wide and 30 cm in length. Rf power was provided to the reactor through two concentric rings located around the exterior of the reactor. The rf circuitry included function and pulse generators, rf amplifier, frequency counter, and matching network (with wattmeter) to minimize reflected power. An oscilloscope was employed in tuning the rf circuit under pulsing conditions. All reactor variables such as rf frequency (13.56 MHz), monomer pressure (0.43 torr), flow velocity (9.6 $\text{cm}^3\ \text{min}^{-1}$), rf power (300 W), and positioning of the substrate samples in the reactor were held constant. In this way, the influence of the variable rf duty cycle on molecular composition of the films obtained was isolated. Substrates employed were mainly polished silicon and KCl

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