selective hydrocarbon oxidation catalyst.

(G) One learns from the coordination chemistry[22] of *fac*-LMO_3 complexes of M = Mo, W that the propensity[21] of "zeolate"-ligated MO_3 to form dimeric units in the case of $M = W^{6+}$ and monomeric units in the case of $M = Mo^{6+}$ could be related to the anticipated greater intrinsic lability (reactivity) of the W^{6+} relative to the Mo^{6+} monomeric $(ZO)\cdots MO_3\cdots(NaOZ)$ coordination sites. In this way, one can satisfactorily rationalize the following:

(i) The formation of dimeric $(ZONa)\cdots O_2W(\mu\text{-}O)_2WO_2\cdots(NaOZ)$ from *trans*-$(ZONa)\cdots(OC)W(CO)_4(CO)\cdots(NaOZ)$ yet monomeric $(ZO)\cdots MoO_3\cdots(NaOZ)$ from *trans*-$(ZONa)\cdots(OC)Mo(CO)_4(CO)\cdots(NaOZ)$;

(ii) The thermal oxidation of monomeric $(ZO)\cdots WO_2\cdots(NaOZ)$ to dimeric $(ZONa)\cdots O_2W(\mu\text{-}O)_2WO_2\cdots(NaOZ)$ yet monomeric $(ZO)\cdots MoO_2\cdots(NaOZ)$ to monomeric $(ZO)\cdots MoO_3\cdots(NaOZ)$;

(iii) The formation of dimeric $(ZONa)\cdots O_2W(\mu\text{-}O)WO_2\cdots(NaOZ)$ from dimeric $(ZONa)\cdots O_2W(\mu\text{-}O)_2WO_2\cdots(NaOZ)$, yet the nonexistence of Mo^{5+}–Mo^{5+}, or Mo^{6+}–Mo^{6+} analogs.

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Effect of Chain Length on the Conductivity of Polyacetylene. Potential Dependence of the Conductivity of a Series of Polyenes Prepared by a Living Polymerization Method

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The controlled ring-opening metathesis polymerization of 7,8-bis(trifluoromethyl)tricyclo[4.2.2.0^{2,5}]-deca-3,7,9-triene has been employed to prepare soluble polymers of low polydispersity that are precursors to polyenes. Films of these precursor polymers have been cast from solution onto platinum microelectrode arrays and have been heated to form films of polyacetylene in the molecular weight range 400–6500. These films have been characterized by in situ measurements of conductivity as a function of electrochemical potential in liquid SO_2/electrolyte. The results show a steady increase in conductivity with average chain length for samples with chain lengths in the range 11–60 double bonds, above which conductivity levels off as chain length continues to increase. All samples exhibit a finite potential window of conductivity which increases in width in the range 11–60 double bonds and does not change further with increasing chain length.

Introduction

The dependence of conductivity upon conjugation length is an issue of fundamental importance in the study of conducting polymers.[1] There is a great deal of interest in determining the relationship between properties observed for short polyenes and those for polyacetylene, an "infinitely long" polyene. The relative importance of intra- and intermolecular mechanisms of charge transport in these materials has been the subject of some discussion.[2,3] Studies of the conductivity of discrete polyenes containing between one and six double bonds showed that they are poor conductors and that there is little improvement in conductivity over this range of conjugation lengths.[4] Some studies of polyacetylene have indicated a strong dependence of conductivity on molecular weight,[3,5] while others have indicated no such correlation.[6] However, these previous studies have been limited by the difficulties associated with preparing polyacetylene in a controlled fashion using classical catalyst systems. The conjugation length in highly conducting polyacetylene has been estimated to lie in the range 20–50 double bonds.[7-10]

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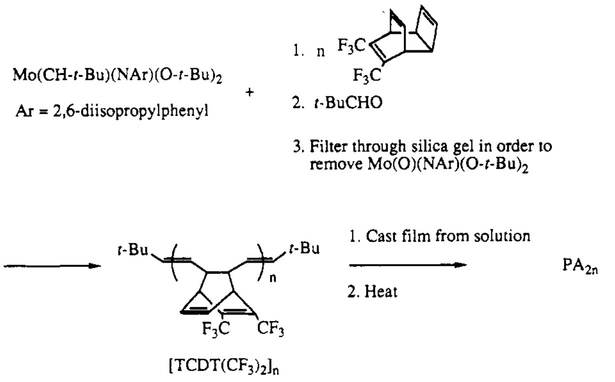
Scheme I. Controlled ROMP of $TCDT(CF_3)_2$ by $Mo(CH\text{-}t\text{-}Bu)(NAr)(O\text{-}t\text{-}Bu)_2$ To Give PA_{2n}



Therefore, the most interesting polyenes should lie between the short, discrete polyenes and the higher molecular weight polyacetylenes that have been accessible by previous synthetic routes.

It is now possible to prepare precursors to polyenes and polyacetylenes that have low polydispersities by a living ring-opening metathesis polymerization (ROMP).[11,12] We reported previously that a relatively low molecular weight sample of polyacetylene (molecular weight = 3200) prepared by this new route exhibited conductivity (after electrochemical oxidation in liquid SO_2/electrolyte) of the same order as that typically reported for much higher molecular weight samples of unoriented Durham polyacetylene ($\sim 10\ \Omega^{-1}\ cm^{-1}$).[13] In addition, this polyacetylene sample also exhibited a finite window of high conductivity as a function of electrochemical potential, as had been previously observed for a number of other conducting polymers.[14,15] By virtue of our ability to prepare polyacetylene samples of low polydispersity, as well as our ability to make in situ measurements on conductivity for oxidized polymer films, we are now able to report the effect of varying the average chain length on conductivity for a series of polyene and polyacetylene samples that span the range of molecular weights from 400 to 6500. We also disclose a design for a macroscopic array of independently addressable microelectrodes and their use in measuring the potential dependence of conductivity for solution cast polymers.

Results

Synthesis of Polyacetylene Samples. The synthetic route used to prepare poly[7,8-bis(trifluoromethyl)tricyclo[$4.2.2.0^{2,5}$]deca-3,7,9-triene ($[TCDT(CF_3)_2]_n$) is outlined in Scheme I. We have shown previously that this process is living and yields polymers of low polydispersity (sample polydispersities: n equivalents/PDI = 30/1.16; 60/1.15; 150/1.11; 250/1.18) from which di-*tert*-butyl capped polyenes can be formed upon heating.[11] Therefore we are able to prepare samples of the precursor polymer, $[TCDT(CF_3)_2]_n$, where n can be varied over a range of desired molecular weights. Films are then cast from solutions of $[TCDT(CF_3)_2]_n$ polymers onto the surface of platinum electrodes for electrochemical characterization (see following section). The electrode array is then heated to 120 °C for approximately 5 min in order to convert the films of the precursor polymer into films of polyacetylene that we will designate PA_{2n}, in keeping with the number of double bonds per polymer chain that are produced upon heating (two from each monomer). Although the average length and dispersity of the *precursor* polymer chains are known, we do not know the *exact* molecular structure of the polyacetylene that is generated, i.e., the nature and extent of cross-linking, if any, between polyacetylene chains.

Table I. PA_{2n} Samples

$[TCDT(CF_3)_2]_n$	PA_{2n}	MW
$[TCDT(CF_3)_2]_{7.5}$	PA_{15}	500
$[TCDT(CF_3)_2]_{10}$	PA_{20}	600
$[TCDT(CF_3)_2]_{15}$	PA_{30}	900
$[TCDT(CF_3)_2]_{20}$	PA_{40}	1150
$[TCDT(CF_3)_2]_{25}$	PA_{50}	1400
$[TCDT(CF_3)_2]_{30}$	PA_{60}	1650
$[TCDT(CF_3)_2]_{60}$	PA_{120}	3200
$[TCDT(CF_3)_2]_{125}$	PA_{250}	6600

Samples of PA_{2n} ($2n$ = the nominal conjugation length) that were investigated are listed in Table I. The molecular weight values that are shown are the theoretical average nominal molecular weights for the samples in the *absence* of cross-linking or other side reactions. (The molecular weights include the *t*-Bu groups at the chain ends.) A di-*tert*-butyl-capped discrete polyene containing 11 double bonds also was prepared and isolated by methods described previously.[11] This sample will be called the 11-ene in order to distinguish it from the samples that contain a distribution of chain lengths. The shorter samples (11-ene, PA_{15}) formed reddish colored films, while PA_{30} and PA_{40} formed dark films with a bluish cast. PA_n where $n \geq 60$ formed shiny films with colors that ranged from black to silver. Film thicknesses were estimated (as described in the Experimental Section) to be between 0.03 and 0.19 μm. Although most of the samples that will be described here are more accurately called oligomers rather than polymers, they will all be referred to as polyacetylene samples for the sake of convenience. The thermally generated films have not been oriented (e.g., by stretching) and are expected to contain a mixture of cis and trans double bonds prior to doping.

Microelectrode Arrays. The platinum electrode arrays used in these studies are composed of eight individually addressable platinum electrodes on an insulating substrate (Si_3N_4), as shown in Figure 1. Four of the electrodes (numbers 1, 4, 5, and 8 in Figure 1) are composed of 4136 interdigitated "teeth", each 4 μm wide and 46 μm long, that are separated from the neighboring electrodes by 4 μm, and branch from "spines" 50 μm wide and 1.5 mm long. In addition, there are four individually addressable band microelectrodes in the center of the array (numbers 2, 3, 6, and 7 in Figure 1), each 1.5 mm long, 4 μm wide, and separated from one another by 4 μm. These eight electrodes, when configured in a fully interdigitated manner (see below), approximate two linear electrodes over 21 cm long, separated by 4 μm, in a bounded working area 1.5 mm by 2.3 mm. Arrays of closely spaced individually addressable electrodes have proven useful for in situ measurements of conductivity of polymer films.[16] The arrays described here are particularly versatile in that the eight individual electrodes may be configured in a variety of arrangements with respect to one another allowing the study of both highly conducting as well as relatively in-

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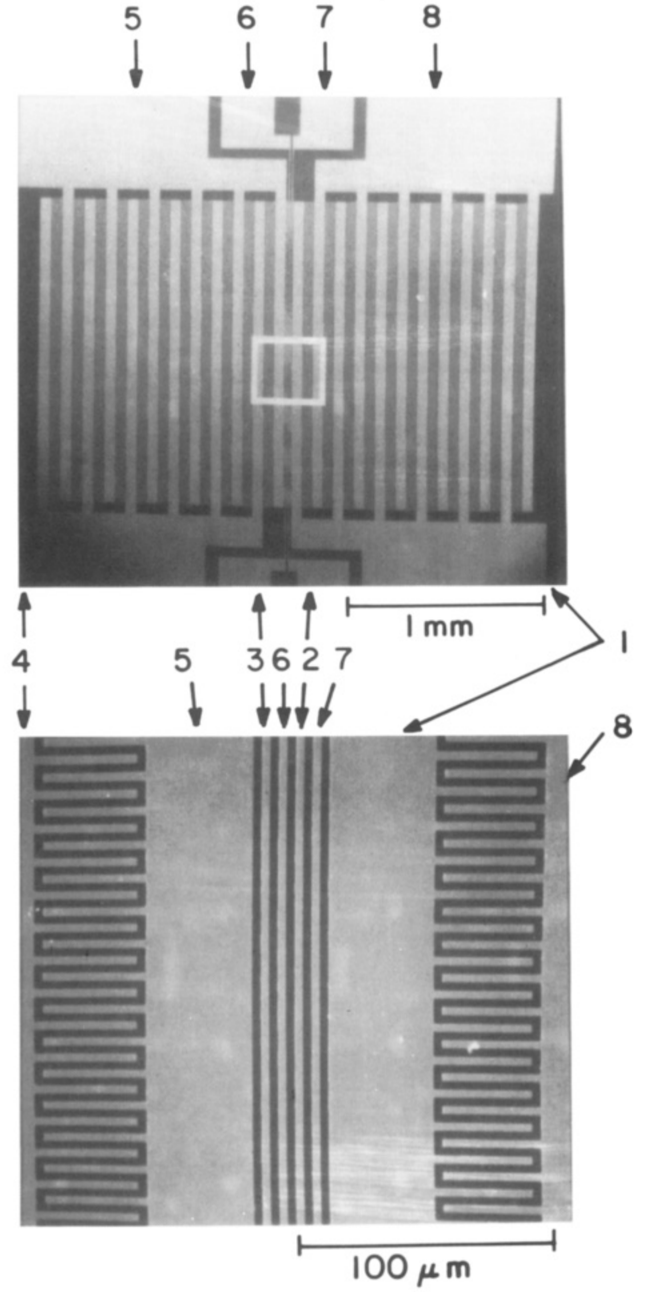
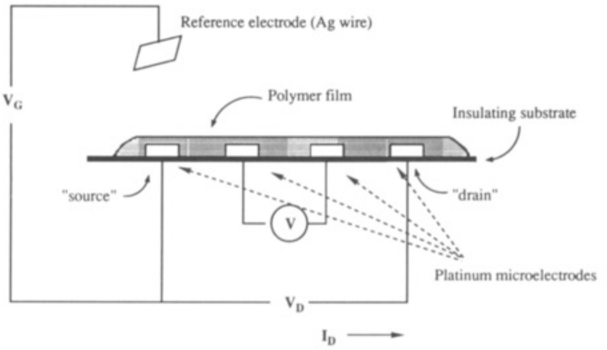


Figure 1. Scanning electron micrographs of a macroscopic interdigitated array of Pt macro- and microelectrodes. Top: whole array with bonding pads numbered. Bottom: magnification of white bordered area from top micrograph with electrodes numbered as in top.

sulating samples. Fabrication of the arrays is described in the Experimental Section.

In a typical experiment two electrodes, labeled the "source" and "drain" were connected by a film of a conducting polymer, and a fixed potential difference, V_D, the drain voltage, was maintained between the two (see Scheme II). At the same time, the gate potential, V_G, of the two electrodes was varied with respect to a reference electrode. As V_G was varied, the degree of oxidation of the polymer film changed. As the film was oxidized ("p-doped") the polymer became conducting and significant current began to flow between the source and drain electrodes. This drain current, I_D, was proportional to the conductivity of the material under investigation. A plot of I_D vs V_G gave the relative conductivity of the polymer as a function of its electrochemical potential. (The middle electrodes were used for a four point probe measurement of conductivity, as described later). The small distances between the electrodes and the use of thin polymer films results in amplification of drain currents relative to faradaic or gate currents at relatively fast scan rates. It is advantageous to use the fastest scan rate at which good amplification can be obtained and at which the polymer film can maintain electrochemical equilibrium with the electrode, in order that the highly oxidized polymer has less opportunity to chemically degrade.

Scheme II. Configuration for in Situ Potential-Dependent Measurement of Conductivity



For highly conducting samples, it is important to be certain that the measured resistance does not include the resistance of the platinum leads themselves. Thus, to obtain maximum source-drain separation, electrodes 1 and 8 together are designated as the source and electrodes 4 and 5 together are designated as the drain; the remaining electrodes (2, 3, 6, and 7) are used for an in situ four-point probe measurement of conductivity (see Experimental Section). Drain currents are much larger than gate currents for highly conducting materials.

For relatively insulating materials, it is reasonable to assume that all measured resistance arises from the polymer itself. In these cases, electrodes 1–4 taken together are designated as the source while electrodes 5–8 together are designated as the drain; in this configuration, the device is said to be fully interdigitated. This allows for the greatest amplification of the relatively small drain currents obtained for such samples. Actual conductivities may then be calculated as described in the Experimental Section.

Liquid SO_2/electrolyte (typically $[(n\text{-Bu})_4N]AsF_6$ or $[(n\text{-Bu})_4N]PF_6$) was chosen as the solvent system for these studies because of the extremely positive potentials that can be accessed (+4.5 V vs SCE).[17-20] It is also a good choice for experiments in which highly oxidized species are being investigated, due to the low nucleophilicity of SO_2.[14]

Electrochemical Measurements. We previously reported that PA_{120} (MW = 3200) exhibits a finite window of conductivity as a function of electrochemical potential upon oxidation in liquid SO_2/electrolyte.[14] Similar experiments carried out on samples of the polyacetylene films listed in Table I reveal a number of interesting similarities and differences. The I_D–V_G traces for three samples are shown in Figure 2. Note that the current scales are different for each sample. For the samples in Figure 2a,b, the microelectrode arrays were configured in the fully interdigitated fashion described above (electrodes 1–4 operating as the source, 5–8 operating as the drain) in order to afford maximum amplification maximum amplification.

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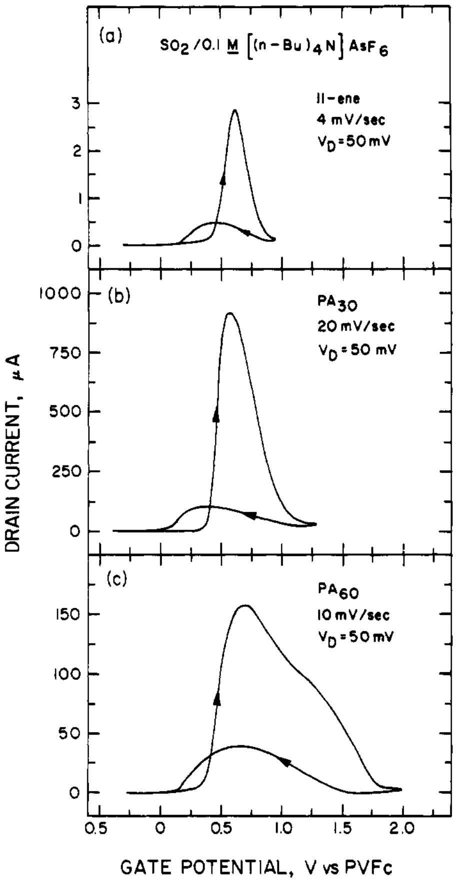

Figure 2. I_D–V_G characteristics for PA_{2n} films on interdigitated Pt electrode arrays in SO_2/0.1 M [(n-Bu)$_4$N]AsF$_6$ at −70 °C: (a) 11-ene (film contains 3 × 10^{-8} mol of double bonds); (b) PA_{30} (film contains 3 × 10^{-8} mol of double bonds); (c) PA_{60} (film contains 6 × 10^{-9} mol of double bonds).

For the sample shown in Figure 2c, the array was configured with electrodes 1 and 8 as the source and electrodes 4 and 5 as the drain since the drain current for this sample was relatively large. All samples, regardless of nominal chain length, exhibit a finite potential-dependent window of conductivity. In addition, the drain currents measured on the negative sweeps are consistently lower than those measured on the positive sweeps, an effect that has been observed previously for other conducting polymers.[14] For all samples, the entire trace (positive and negative sweeps taken together) may be reproduced in subsequent scans, indicating that this effect cannot be ascribed to irreversible decomposition at the most positive potentials. Currents measured in each subsequent scan typically are approximately 10% lower than in the previous scan but in all other respects are identical.

The difference in the magnitude of the drain currents on the positive and negative sweeps appears to be magnified for the shorter samples (compare Figure 2a,b to Figure 2c or to data for PA_{120}[13]). This is somewhat misleading. It has been found that the conductivity of the samples varies significantly as a function of molecular weight, as will be discussed below. In fact, the longer polyacetylene samples are so highly conducting that the resistance associated with the platinum electrodes approaches or is greater than the resistance of the polymer. Therefore the drain currents measured on the positive sweeps for the longer polyacetylene samples are limited by the platinum device resistance more than the drain currents on the negative sweeps. Thus, the relative magnitudes of the drain currents for the positive and negative sweeps observed in the I_D–V_G trace for 11-ene or PA_{30} are believed to be more accurate than the relative heights observed for the longer samples. (The device resistance has been taken into account in the calculations of maximum conductivity for each sample.) It is also interesting to note that if the I_D–V_G scan is reversed at somewhat less positive potentials, before the drain current decreases significantly, the drain currents measured on the negative sweeps are much larger and may in fact be larger than the currents measured on the positive sweep (see Figure 3).

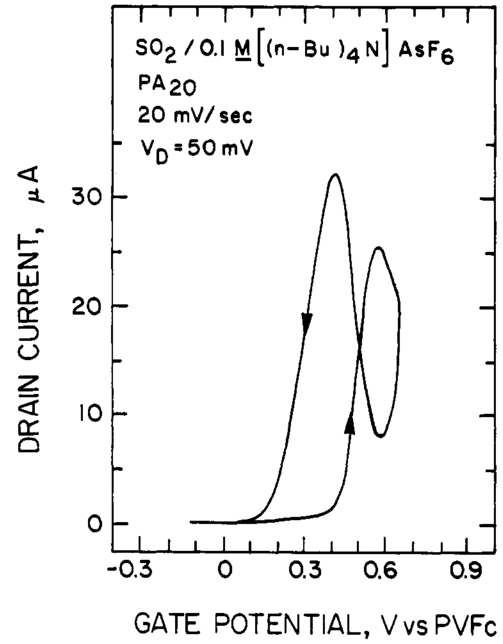

Figure 3. I_D–V_G characteristic for a PA_{20} film containing 6 × 10^{-9} mol of double bonds on an interdigitated Pt electrode array in SO_2/0.1 M [(n-Bu)$_4$N]AsF$_6$ at −70 °C.

Table II. Width of Windows of Conductivity (V) and Maximum Conductivity (Ω^{-1} cm^{-1}) Obtained for PA_{2n} Samples upon Oxidation

PA_{2n}	av width of window,[a] V	av max conductivity, Ω^{-1} cm^{-1}
11-ene	0.38	1.7 × 10^{-5}
PA_{15}	0.47	1.6 × 10^{-4}
PA_{20}	0.50	1.0 × 10^{-3}
PA_{30}	0.51	1.1 × 10^{-1}
PA_{40}	0.63	3.0 × 10^{-1}
PA_{50}	0.91	1.6
PA_{60}	1.22	9.7
PA_{120}	1.18	45
PA_{250}	1.28	72

[a] The width of the window is defined as the region in which the conductivity is at least 20% of the maximum.

All the I_D–V_G traces in Figures 2 show scan-rate-independent hysteresis. Hysteresis is a characteristic of all potential-dependent processes in conducting polymers and is believed to be a consequence of reversible structural changes in the polymers accompanying charge injection.[14,21,22] For all samples, the change in conductivity as the polymer is oxidized from the neutral state to the maximally conducting state is much greater than that when the polymer is further oxidized to the positive potential limit. For example, in PA_{60} (Figure 2c) the change in conductivity on the negative potential side of the I_D maximum is at least 6 orders of magnitude, whereas it is

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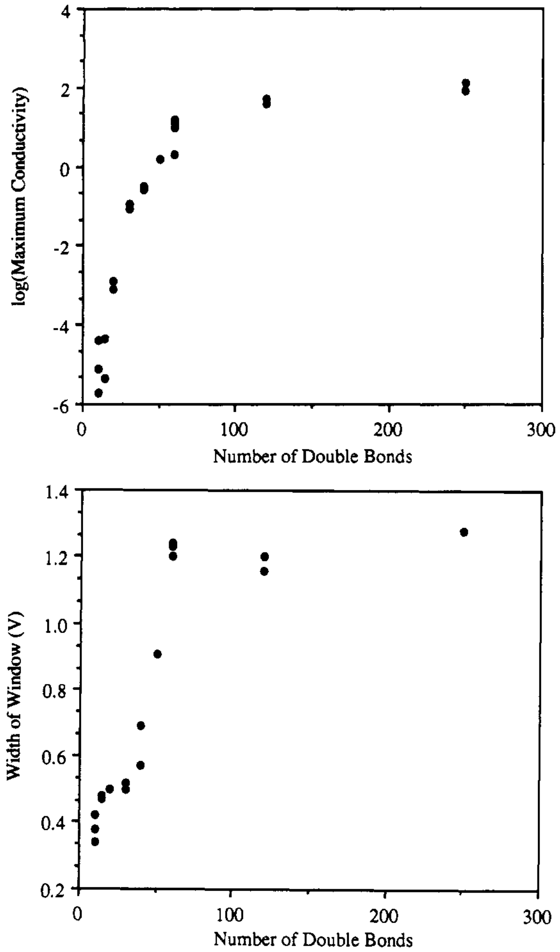

Figure 4. (top) Plot of log (maximum conductivity) vs number of double bonds for all experiments performed on 11-ene and PA_{2n} samples. (bottom) Plot of width of potential window of high conductivity vs number of double bonds.

only about 3 orders of magnitude on the positive side. The positive sweep limit is the potential positive of which chemical degradation occurs relatively rapidly. Results such as those shown in Figure 2 were obtained for all the samples listed in Table I and are summarized in Table II. The values listed for the conductivities given are the averages of several experiments in most cases. We have defined the width of the window of high conductivity as the width of the potential region in which the conductivity is at least 20% of the maximum conductivity. An important point is that for the 11-ene and PA_{15}, although the conductivities upon oxidation are quite low and the potential windows of high conductivity are narrow, the behavior of these materials is similar to that of the higher molecular weight materials in all other aspects of the I_D–V_G characterization. The conductivities that we have measured for these samples upon doping are 5–6 orders of magnitude greater than the conductivities that have been reported for similar undoped polyenes.[23] Unfortunately, it was not possible to study shorter samples of discrete unsubstituted polyenes because they become soluble in SO_2 upon oxidation.

Two trends are apparent from a comparison of the I_D–V_G's in Figure 2 and the data in Table II. First, maximum conductivity clearly correlates with average chain length. This is most obvious from Figure 4a, in which log (maximum conductivity) is displayed against the average number of double bonds of all samples studied. The maximum conductivity changes significantly in the region of lower molecular weight but relatively slowly above PA_{60}. It might be argued that the relatively low conductivities measured for the lower molecular weight samples can be ascribed to an effective dilution of the conjugated portion of the polymer chains with respect to the aliphatic portion, thereby allowing less effective charge transfer through the material. For the 11-ene, for instance, the end groups account for more than 25% of the weight of the sample. However, we have examined samples of polynorbornene/polyacetylene diblocks[11] in which the polynorbornene portion accounts for ~55% (PA_{60}–NBE_{20}) and ~70% (PA_{30}–NBE_{20}) of the total polymer mass and found that there was no significant effect of the polynorbornene block on conductivity compared to conductivities of the "undiluted" PA_{60} and PA_{30}, respectively. Previous studies of polynorbornene/polyacetylene diblocks prepared by the same synthetic method that has been used here have shown no evidence for microphase separation. Calculations indicated that microphase separation in this system would be expected only for diblocks of much higher molecular weights than those studied here.[24] The maximum conductivities of 11-ene and of PA_{120} did not vary significantly as a function of temperature in the range between −70 and −10 °C.

The second trend apparent from the I_D–V_G characterization of the polymers is a correlation between average chain length and the width of the potential window of high conductivity, as shown in Figure 4b. Just as in the case of the maximum conductivity, the width of the window of high conductivity changes dramatically at lower molecular weights but does not change significantly above PA_{60}. Studies of other conducting polymers have shown that the relative width of the window correlates with the maximum conductivity measured for those materials.[14] In general, the greater the width of the window, the more conducting the polymer. The data presented here reveal the same trend for polyacetylene; the width of the window increases with the maximum conductivity of the sample, which in turn varies with the average molecular weight of the sample.

Figure 5 shows the cyclic voltammograms for the 11-ene, PA_{30}, and PA_{60}. All cyclic voltammograms share certain features. The main peaks are found at roughly the same potentials in all samples. The large peak splitting between the main anodic and cathodic peaks is analogous to what has been reported previously for high molecular weight polyacetylene[13,25–28] and is a characteristic of conducting polymers in general.[14,29,30] The primary anodic peak observed in the cyclic voltammograms coincides with the region of high drain currents observed in the corresponding I_D–V_G traces. The peak splitting in the cyclic voltammograms coincides with the hysteresis observed in the I_D–V_G's and is also found to be independent of scan rate. It is particularly interesting to find that even short oligomers display cyclic voltammetry that is essentially the same as

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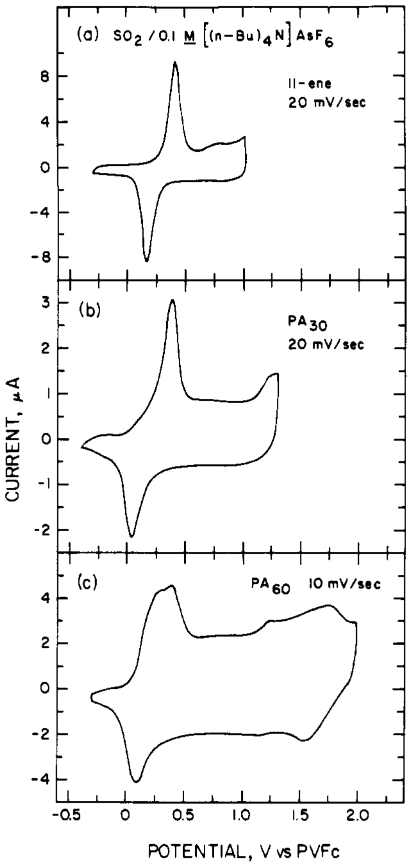

Figure 5. Cyclic voltammograms for PA_{2n} films on Pt electrodes in SO_2/0.1 M $[(n\text{-}Bu)_4N]AsF_6$ at −70 °C: (a) 11-ene (film contains 3×10^{-8} mol of double bonds); (b) PA_{30} (same film as in Figure 2b); (c) PA_{60} (same film as in Figure 2c).

that observed for polyacetylene. This, in addition to the I_D–V_G characteristics, suggests that the electronic structure is similar in all samples, regardless of molecular weight. Furthermore, films of β-carotene, a methyl-substituted polyene containing 11 double bonds, although somewhat soluble in SO_2, were sufficiently persistent to show cyclic voltammetry *unlike* that of polyacetylene (or the 11-ene), i.e., behavior more like that of an ordinary reversible redox reagent, consistent with its known solution behavior.[31]

The cyclic voltammograms are reproducible over the potential limits shown, and there is little evidence for decomposition of the samples. The anodic peak at ~1.1 V for PA_{30} in Figure 5b is due to an impurity. However, the anodic and cathodic peaks for PA_{60} in the 1.2–1.9-V region (Figure 5c) are similar to those previously reported for PA_{120} and correlate with large changes in conductivity (Figure 2c), as has been reported previously for other highly oxidized conducting polymers.[14] For all samples, there is significant faradaic current at the positive potential limit which is correlated with conductivities greater than those measured for the neutral polymers (see above).[14] Further oxidation is precluded by the onset of rapid sample degradation.

Integration of the cyclic voltammograms to the potential of maximum conductivity also provides some interesting results. For samples of PA_{2n} where $2n \geq 30$, the maximum conductivity is found to occur when the polymer is oxidized to the extent of ~0.1 electron per double bond. These results are in agreement with theoretical predictions as well as results from chemical doping studies which have indicated that maximum conductivity for polyacetylene is expected to occur at a ~10% doping level.[32,33] However, integration of the cyclic voltammograms to the potential of maximum conductivity indicates that the 11-ene is only oxidized by ~0.02 electron per double bond, and in the case of PA_{15} and PA_{20} by ~0.04 electron per double bond. These results did not change at lower coverages or scan rates, and there was no evidence for significant dissolution of material. They indicate oxidation to an extent of less than one electron per chain, in contrast to predictions that nine double bonds should be sufficient to sustain a positively charged polaron.[34] To test whether portions of these films were electrochemically inaccessible, we examined films of the 11-ene cast from solutions in which I_2 had been dissolved (0.3 mol of I_2/mol of 11-ene). Integration of cyclic voltammograms of samples prepared in this fashion indicated that much more of the film could be accessed (the electron count increased by approximately a factor of 3), while the maximum conductivities were no different than those of the 11-ene alone.

Discussion and Conclusions

The most important finding is that the conductivity and the width of the conductivity window change most dramatically in the range of molecular weights between 400 and 1650 (11-ene to PA_{60}). Above a molecular weight of 1650, conductivity improves relatively slowly and the width of the window does not vary significantly. For samples that contain nominally fewer than 60 double bonds, the variation in conductivity is a smooth one. There is no evidence for a sudden discontinuity in the chain-length-dependent evolution of properties observed for samples in this molecular weight range. All samples exhibit similar cyclic voltammetric behavior, i.e., all have the characteristic large potential difference between anodic and cathodic peaks, and the potentials at which these peaks are found are relatively constant. The I_D–V_G behavior also is relatively constant over this molecular weight range. In all respects, the oligomers and polymers studied here have potential-dependent characteristics of classical polyacetylene[13] and lead us to conclude that the electronic structure of all these samples is similar. This is highlighted by the contrast between the behavior of our samples and that of β-carotene, a methyl-substituted polyene, for which the redox behavior and low conductivity indicate a much more localized electronic structure. In addition, the conductivity of the 11-ene and PA_{120} are both essentially independent of temperature between −70 and −10 °C. This implies that the mechanism of conductivity in 11-ene bears some similarity to that in polyacetylene, at least in that it is significantly different from ordinary redox conduction via self-exchange between highly localized charge sites, as in polyvinylferrocene,[35] for which we would expect to observe a change in conductivity (D_{CT}) of at least an order of magnitude over this temperature range.[36]

For polyenes longer than PA_{60} conductivities approach those previously reported for unoriented samples of Durham route polyacetylene. These results suggest that polyenes containing 60 double bonds possess fundamental

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properties of high molecular weight polyacetylene. It is interesting to note that the conjugation length in polyacetylene has been estimated to lie in the range 30–50 double bonds.[7-10]

For samples with a molecular weight higher than that of PA_{60}, we observed only a negligible increase in conductivity and essentially no change in the width of the potential window of high conductivity. However, the maximum conductivities that we have measured are still significantly lower than the values that have been reported for samples of highly ordered polyacetylene prepared by different synthetic methods.[37] Cast films of unoriented Durham-route polyacetylene are known to be substantially less crystalline than those prepared by other methods, and therefore we cannot rule out the possibility that we might observe a greater dependence of conductivity on MW for samples above PA_{60} if we were able to orient our films. However, previous studies of poly(1,4-dialkoxy-*p*-phenylene ethynes) have suggested that while bulk conductivity is a macroscopically determined property, the width of the window of high conductivity is determined on the molecular level.[38,39] Therefore, the negligible increase in the width of the window above PA_{60} suggests that chain length has little effect above PA_{60} and that intermolecular charge transport plays the major role in determining the maximum conductivity for high MW polyacetylene.

For lower molecular weight samples, the relative importance of intramolecular charge transport becomes significant. We observe a strong dependence of the conductivity and of the width of the window of high conductivity on molecular weight for samples up to PA_{60}. In addition, the homogeneous dilution of the conjugated polymers with a nonconductive material (in the absence of microphase separation) does not significantly affect our measurements. We feel that these results indicate a continuous evolution of charge delocalization as a function of molecular weight and therefore tend to support the hypothesis that intramolecular charge transport plays a significant role in determining the conductivity of these lower molecular weight samples.

Experimental Procedures

General Procedures. All reactions were carried out under inert atmosphere (nitrogen or argon) in a Vacuum Atmospheres glovebox or by standard Schlenk techniques. Mo(CH-*t*-Bu)(NAr)(O-*t*-Bu)$_2$[40] and TCDT(CF$_3$)$_2$[11] were prepared by routes described elsewhere. Pivaldehyde (Aldrich) was distilled and passed over alumina before use. Silica Gel (Merck grade 60, 3 × 40 cm) was dried (at ~130 °C) in vacuo overnight. Solvents were dried under N_2 by standard procedures and degassed before use. SO_2 was obtained from Matheson and was bubbled through concentrated sulfuric acid and condensed onto P_2O_5, followed by vacuum transfer onto basic alumina. The SO_2 was stored over alumina at −77 °C and was vacuum transferred into the electrochemical cells as needed. $[(n\text{-Bu})_4N]AsF_6$ was prepared from $[(n\text{-Bu})_4N)]Br$ and $LiAsF_6$ and was recrystallized from acetone/H_2O. $[(n\text{-Bu})_4N]PF_6$ was recrystallized from ethyl acetate. Electrolytes were dried at 10^{-2} Torr at 120 °C. For all electrochemical experiments platinum mesh was used as the counterelectrode, and an oxidized silver wire was used as the quasi-reference electrode; a platinum electrode derivatized with polyvinylferrocene was used for the in situ determination of the reference potential.

Platinum flag electrodes were used for cyclic voltammetric experiments. Platinum electrode arrays were fabricated and mounted as described previously (Figure 1).[41,42] Photolithography for these devices was performed using a GCA MANN Model 4800 DSW Wafer Stepper and a GCA Model 1006 Wafertrac. Metallization was done on a Sloan e-beam evaporator. All arrays and flag electrodes were cleaned by O_2 plasma etching at 10^{-1} Torr and 30 W for 3 min. Pretreatment and characterization of the individual electrodes on the microelectrode arrays was carried out by cycling the individual electrodes in 0.5 M H_2SO_4 between 1.2 and −0.25 V vs SCE as has been described previously.[14]

All electrochemical experiments were carried out in vacuum tight single-compartment cells. The cells were dried, assembled and loaded with electrolyte in an inert atmosphere drybox, and evacuated to ~10^{-5} Torr while heating to 120 °C. The cells were then cooled and opened under inert atmosphere. Samples were then introduced into the cells, and the cells were evacuated to 10^{-5}–10^{-6} Torr. SO_2 was then vacuum transferred into the cells and the experiments were carried out at −77 °C. The final electrolyte concentration was approximately 0.1 M in all cases.

Preparation of Polyacetylene Films. To a solution of Mo(CH-*t*-Bu)(NAr)(O-*t*-Bu)$_2$ (0.005 g, 1.03 × 10^{-5} mol) in 500 μL of THF was added a solution containing *n* equiv of TCDT(CF$_3$)$_2$ (*n* × 2.73 mg, *n* × (1.03 × 10^{-5}) mol) in (*n* × 50 μL) THF. The solution was stirred for 30–75 min, depending on *n*. The living precursor polymer was then capped by addition of excess pivaldehyde (6 μL, 5 × 10^{-5} mol) followed by stirring for approximately 30 min. The solution was then passed through silica gel in order to remove the metal–oxo complex formed during the capping reaction. The polymer solution was then diluted with THF to a total volume of *n* × 0.170 mL. Films were cast directly onto the surface of the electrodes (macro and micro) using 0.25-μL capillary pipettes; 3 × 10^{-8} mol double bonds (assuming that $2n + 1$ mole double bonds are generated per mole of catalyst used) are deposited onto each electrode. The electrodes were then heated in order to induce the retro-Diels–Alder reaction in the $[TCDT(CF_3)_2]_n$ film, i.e., in order to extrude bis(trifluoromethyl)-*o*-xylene and generate the polyene (polyacetylene).

Measurement of Conductivity. Conductivities can be determined using Ohm's law and the relationship between the resistance of a conductor, its resistivity, ρ, and its geometry: $R = \rho l/A$. If I_D and V_G are known, and the dimensions l and A are taken to be the distance between the source and drain electrodes and the cross-sectional area of the polymer normal to the axis of current flow between the two electrodes, respectively, then the conductivity, σ, is obtained from eq 1. The thickness of the polymer film was estimated by assuming a density of 1.0.[43]

$$\sigma = I_D l / V_D A \qquad (1)$$

Film thicknesses were on the order of 0.03–0.19 μm. For relatively insulating samples, the I_D–V_G characteristics were obtained by designating electrodes 1–4 as the source and 5–8 as the drain. This "fully interdigitated" configuration allows for the greatest amplification of the relatively small drain current obtained for samples with low conductivity. For relatively highly conducting samples, electrodes 1 and 8 were designated as the source and 4 and 5 were designated as the drain, in order to minimize the significance of the resistance of the electrodes themselves. In this configuration, all the drain current flows across the four central microelectrodes, 2, 3, 6, 7, in a direction perpendicular to their long axes. Therefore, these microelectrodes can be used to make pairs of four point probe measurements. Highly conducting samples were held at the potential of maximum conductivity while voltages were measured between all possible pairs of the four

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microelectrodes in order to determine the average potential drop per gap.

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Poly(ethylene oxide)-Silicate Intercalation Materials

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Intercalation of poly(ethylene oxide), PEO, into 2:1 charged phyllosilicates (montmorillonite and hectorite) has been investigated. A model for PEO-silicate compounds based on the preservation of the helical structure of the polymer is postulated. The results of IR, NMR, and X-ray diffraction studies support this hypothesis. The resulting materials show good chemical and thermal stability, improving the characteristic ion conductivity of the parent silicates. Typical conductivity values associated with the motion of the intracrystalline cations contained in the poly(ethylene oxide)/montmorillonite materials ranges from 10^{-7} to 10^{-4} S cm^{-1} for PEO/Na$^+$-montmorillonite compounds (400-600 K, measured in a direction parallel to the silicate layers).

Introduction

The ability of poly(ethylene oxide), PEO, to act as solid solvent for different metal salts giving polyelectrolyte materials of great interest in various electrochemical applications, such as solid-state batteries, electrochromic devices, sensors, etc., is widely known.[1-6] Among the factors controlling the ion mobility, the crystallinity of polymers and the nature of the counterion appear to be the most influential features. In this way, inorganic materials such as NASICON or alumina are combined with polymeric oxyethylene compounds giving PEO composite systems with improved mechanical properties and, in some cases, enhancing the inner conductivity of PEO complexes.[7-9]

Conventional PEO salt complexes exhibit ionic conductivity based on both anionic and cationic mobility (ion-pair transport), which can impose limitations for various applications. The capability of certain layer silicates to intercalate a large variety of organic compounds,[10,11] including oxyethylene compounds as crown ethers[12-14] and poly(ethylene glycol),[15-17] opens ways to insert PEO into 2:1 charged phyllosilicates, such as montmorillonite and hectorite. The structure of these silicates consists of layers built up by two tetrahedral silica sheets and a central octahedral sheet of magnesia or alumina (Figure 1). Isomorphous substitutions, mainly in the octahedral sheets, give a negative charge located in the layers which is compensated by cations (exchangeable cations) in the interlayer space. Thus, oxyethylene compounds as intercalates can act as ligands of these interlayer cations, giving rise to stable complexes. These properties have been used to prepare PEO-silicate intercalation materials that we describe in this work.

Preliminary results concerning Li$^+$-montmorillonite intercalated compounds have been published in a previous note[18] which showed promising properties for PEO-composite materials. The silicate matrix constitutes the counterion, and consequently in PEO-silicate materials the conductivity is exclusively restrained to cations of the interlayer region ($t_- = 0$). In addition to this behavior, the layer structure imposes a marked anisotropy, the conductivity in the direction parallel to the *a,b* plane being about 10^3 times greater than the corresponding conductivity determined along the *c* axis, as we reported previously.[18,19]

This paper concerns the study of the intercalation process of PEO (average molecular mass 10^5) in different homoionic montmorillonites and hectorites, describing their structural features and the properties related to its ionic conductivity.

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