Relevant topics for *Chemistry of Materials* include both theoretical and experimental studies that focus on the preparation, characterization, processing, or understanding of materials with unusual or useful properties. Of particular importance are the originality, significance, overall quality, and completeness of the work as well as its relevance to both chemistry and materials science. The last of these considerations, in particular, serves to define the particular focus of this journal and the special niche that it seeks to fill among periodicals in materials science.

Recognizing the international scope and the breadth of the subject, the Editorial Advisory Board of *Chemistry of Materials* has been selected to ensure a strong international representation as well as a broad perspective on the wide range of subjects in materials chemistry. Included on the Advisory Board are over sixty scientists and engineers from academic, industrial, and governmental laboratories in ten different countries. The articles scheduled for publication in the first few issues are illustrative of this broad, international perspective on materials chemistry. Among the topics covered are molecular and polymeric conductors, nonlinear optical materials, thin-film resists, various aspects of solid-state inorganic chemistry including high-T_c superconductors, sol–gel processing, chemical vapor deposition, ceramic precursors, biosensors, colloid chemistry, electronic materials processing, heterogeneous catalysis, and many other subjects at the forefront of current research in materials chemistry. This broad perspective on fundamental research in materials chemistry will continue in the future issues of this journal.

Last but by no means least, I would like to thank those whose efforts have led to the realization of this journal. These efforts began over four years ago with the establishment of a task force to investigate the need for such a journal. The report of this task force and that of the subsequent selection committee for the journal editor have played an important role in the definition of the scope and purpose of *Chemistry of Materials*. During the past year, the dedicated efforts of the Washington, D.C., and Columbus, Ohio, staff of the ACS Publications Division have resulted in the transformation of these ideas into a functioning journal. Special thanks also go to the two Associate Editors, Dennis Hess and Gary Wnek, and the members of the Editorial Advisory Board, who have been called upon frequently in this last year for advice, reviews of manuscripts, and their own papers. Finally, all of the authors who have responded so enthusiastically to our call for papers and the reviewers who have given their time to provide the critical evaluation of the submitted papers deserve the major credit for getting this journal off to such a flying start.

Leonard V. Interrante

Communications

Potential Dependence of the Relative Conductivity of Poly(3-methylthiophene): Electrochemical Reduction in Acetonitrile and Liquid Ammonia

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We report chemically reversible electrochemical reduction of poly(3-methylthiophene) and electrical and optical properties for the reduced material. It is well-known that large increases in conductivity occur upon oxidation of a number of thiophene-based polymers.[1,2] Recently, conducting polymers have been shown to have a finite potential window of high conductivity upon oxidation.[3–5] In the case of poly(3-methylthiophene)[3] oxidation to yield the nonconducting oxidized state requires the use of unusual media to minimize degradation. This result has prompted us to examine poly(3-methylthiophene) at the opposite extreme, reduction, to completely define the potential dependence of conductivity. There are reports of the electrochemical reduction of polythiophene,[6] poly(isothianaphthene),[7] and poly(3-phenylthiophene),[8] but characterization of the reduced polymers has been elusive owing to their rapid degradation.

We present here conditions (low temperature and H_2O-free, CH_3CN/- or NH_3/electrolyte media) for chemically reversible reduction of polythiophenes. It has been shown that NH_3 is an excellent solvent for stabilizing radical anions and dianions,[9–11] and we thought it would be an appropriate solvent for studying the reduced forms of conducting polymers. Our studies have involved use of a vacuum-tight, two-compartment cell.[12,13] The cell was first oven dried and transferred to an inert-atmosphere box for assembly and addition of electrolytes, then removed, and attached to a vacuum line. The electrolytes were dried in situ at elevated temperature until an ultimate vacuum of 10^{-6} Torr was obtained. NH_3 was distilled from Na into the electrochemical cell, or CH_3CN was triply distilled from P_2O_5 into the cell. All potentials are reported versus a Ag wire quasi-reference electrode. We have used the poten-

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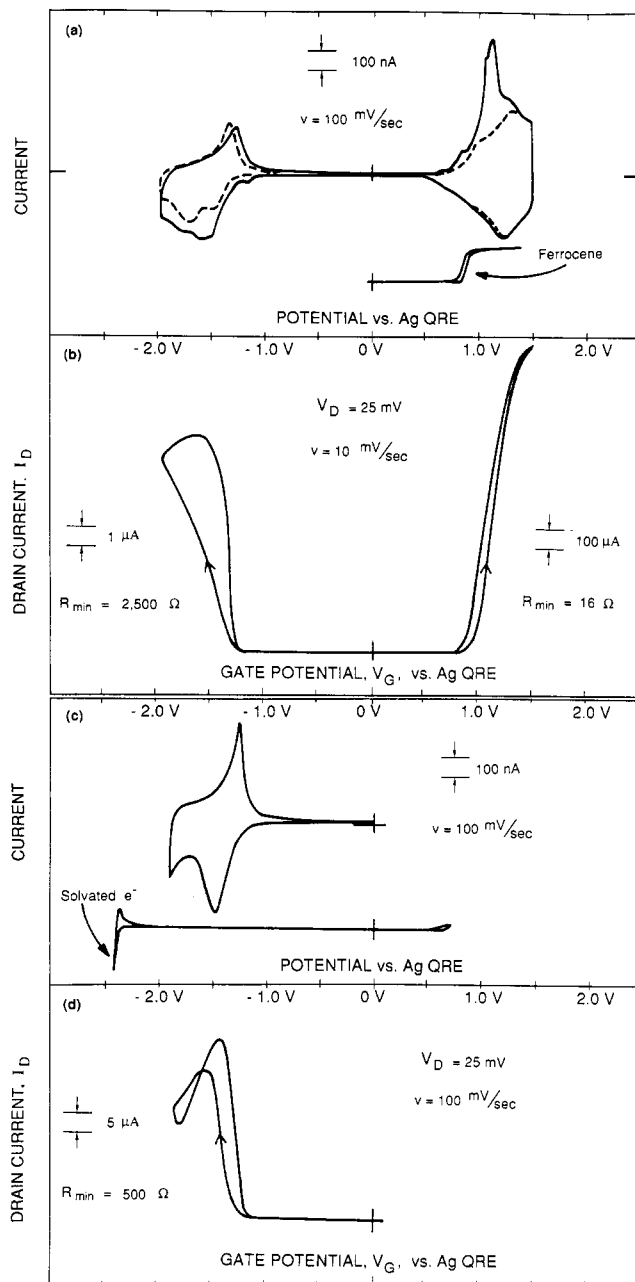
Figure 1. Electrochemical and electronic characterization of poly(3-methylthiophene) at an array of eight Pt electrodes. All data are for a single modified array. Potentials shown are versus a Ag wire, but the potentials of thermodynamically meaningful reference redox couples are shown in the parts a–d. (a) The solid line is the cyclic voltammetry obtained after repetitive cycling in $CH_3CN/0.1$ M $[n\text{-}(Bu)_4N]BF_4$ at -30 °C. The dashed line on the right side of the figure is the cyclic voltammetry obtained if the potential is not swept into a region of cathodic current. The dashed line on the left is obtained if the potential is not cycled into a region of anodic current. The inset shows the steady-state voltammetry of the reference redox couple ferrocene obtained under the same conditions. (b) I_D–V_G characteristic corresponding to (a). (c) Cyclic voltammetry in $NH_3/0.1$ M KCF_3SO_3 at -55 °C. The inset shows the cyclic voltammetry of solvated electrons that were used as a reference redox couple. (d) I_D–V_G characteristic corresponding to (c).

tials for the reversible couples ferrocenium/ferrocene in CH_3CN[14,15] and the solvated electron in NH_3 as in situ reference couples.[16]

Figure 1 shows cyclic voltammetry and relative conductivity vs potential for poly(3-methylthiophene) coated onto a Pt microelectrode array as previously described.[17-20] All data shown in Figure 1 were obtained for the same polymer-modified array so that data obtained with NH_3 and CH_3CN could be compared. The poly(3-methylthiophene)-coated microelectrode array represents a device that can be used to measure the potential, V_G, dependence of the relative conductivity of the polymer as well as the cyclic voltammetry of the polymer.[3] The conductivity at V_G is proportional to the current, I_D, which passes between two microelectrodes having a small voltage, V_D = 25 mV, between them.[3,18,19]

Figure 1 shows cyclic voltammetry of poly(3-methylthiophene) in $CH_3CN/0.1$ M $[(n\text{-}Bu)_4N]BF_4$ at -30 °C and in $NH_3/0.1$ M KCF_3SO_3 at -55 °C. In these two media the cyclic voltammetry is persistent, and characterization of the reduced poly(3-methylthiophene) is possible. We observe that even the slightest detectable trace of H_2O or acid leads to degradation of the reduced form of the polymers studied. Unfortunately, owing to easy oxidation of NH_3, study of the oxidation of poly(3-methylthiophene) is not possible in NH_3/electrolyte. Poly(3-methylthiophene) degrades rapidly in NH_3 or CH_3CN when the potential is scanned more negative than -2.0 V in either CH_3CN or NH_3. In addition to results showing chemically reversible reduction of poly(3-methylthiophene), we have preliminary results for reduction of polythiophene, poly-(3-phenylthiophene), and poly(isothianaphthene) in NH_3 at -55 °C. The reduced forms of these polymers are also durable (i.e., less than 5% decrease in peak reduction current after 50 cyclic voltammograms at 100 mV/s) for excursions to a potential 500 mV negative of the peak current potential.

Fine structure apparent in the voltammogram illustrated in Figure 1a has not previously been reported.[2,3,18] The fine structure on the wave at positive potentials appears only if the potential is first swept into a negative ($\sim$-1.0 V) region where cathodic current flows. Further, if only positive scans are done (e.g., 0 to +1.3 V), then the charge corresponding to oxidation is much less (Figure 1a). Similarly, on the negative scan to -2.0 V, more cathodic charge is observed when the reverse scan is extended into the positive potential regime associated with oxidation of poly(3-methylthiophene) ($\sim$0.6 V). The behavior found is a kind of "charge trapping".[21] The amount of charge "trapped" in the negative scan to -2.0 V is nearly the same (within 10%) as the charge released in the positive excursion to +1.3 V. Tentatively, we attribute the charge trapping to electrons isolated from the electrode by intervening polymer near the electrode that becomes insulating when the potential is moved from -2.0 to -0.5 V. Movement of the potential to a region where the polymer is oxidized releases the electrons, because the oxidized polymer is very conducting. The inability to scan positive

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in NH$_3$ rules out investigation of charge trapping in this medium, but the cyclic voltammetry at negative potentials shows chemically reversible reduction in NH$_3$. Compared to the CH$_3$CN medium, the cyclic voltammogram in the NH$_3$ medium shows larger currents and less hysteresis.

Figure 1b illustrates the I_D–V_G characteristic[3,18,19] for poly(3-methylthiophene) in CH$_3$CN at –30 °C. The "charge trapping" observed in the cyclic voltammetry can be correlated with small changes in both the onset of conductivity (<100 mV) and magnitude of conductivity (~10–20%), but the essence of the I_D–V_G characteristic is illustrated in Figure 1b. We have discussed the I_D–V_G characteristic for positive V_G (oxidation) in previous reports.[3,18] Here we concentrate on the differences between the negative and positive V_G excursions. The maximum conductivity observed upon reduction is at least 100 times smaller than upon oxidation.[22] This is in rough agreement with the differences reported previously for reduced and oxidized polythiophene films.[6] The hysteresis for the negative scan of V_G is highly scan-rate dependent, while for the positive scan of V_G the hysteresis is largely insensitive to scan rate. This likely indicates slow charge compensation of the reduced polymer by the bulky (n-Bu)$_4$N$^+$ cation, especially at the reduced temperature employed for these experiments. Greater hysteresis is also expected for the more resistive form of the polymer.

Figure 1d shows the I_D–V_G characteristic in NH$_3$ at –55 °C. Compared to the CH$_3$CN results, the NH$_3$ data show a well-defined peak in conductivity at ~–1.5 V. The absolute conductivity in NH$_3$ appears to be higher than in CH$_3$CN, consistent with the greater amount of charge injected based on the differences in the cyclic voltammetry. The differences (kinetics and degree of reduction) in CH$_3$CN and NH$_3$ are likely attributable to differences in electrolyte used, but intrinsic differences in the two solvents may also play a role. We suggest that the observed increase and then decrease in conductivity of poly(3-methylthiophene) as it is reduced are due to partial filling and then complete filling of the conduction band, in analogy to previous work showing conduction to be greatly diminished by depleting the valence band of carriers.[3] The region of high conductivity of reduced poly(3-methylthiophene) appears to be ~1 V, ~0.3 V less than for the oxidized form of poly(3-methylthiophene), which has significantly higher maximum conductivity. This finding is consistent with the notion that higher conductivity is associated with greater delocalization in broader bands.[23]

The ruggedness of reduced poly(3-methylthiophene) in NH$_3$ at low temperature allows investigation of its optical properties on an optically transparent electrode.[24] The neutral form of the polymer in NH$_3$ at –33 °C shows an absorbance maximum at 486 nm, as reported for measurements in CH$_3$CN.[25] Upon reduction the 486-nm absorption declines, and there is growth in absorption in the near-IR with reasonable preservation of an isosbestic point at ~600 nm upon reduction to –1.8 V. These spectral changes are very similar to those found upon *oxidation* of the polymer in CH$_3$CN.[25] Oxidized and reduced polythiophene are also reported to have similar optical prop-

erties.[6] Similarity in the optical properties of the oxidized and reduced forms of the polymers is surprising. Studies are under way to examine the optical properties for the entire range of potentials where poly(3-methylthiophene) is durable, to determine the nature of differences in optical properties of the fully reduced and fully oxidized materials.

To summarize our new findings, low-temperature, nonaqueous media can be used to study the reduced form of poly(3-methylthiophene) revealing a finite potential region of high conductivity, ~1 V, centered at ~–1.5 V. The maximum conductivity is at least 100 times less than that of the oxidized form when measured in CH$_3$CN/0.1 M [(n-Bu)$_4$N]BF$_4$ at –30 °C. In NH$_3$/0.1 M KCF$_3$SO$_3$ at –55 °C the maximum conductivity of the reduced form is higher than in CH$_3$CN. The optical spectrum of reduced poly(3-methylthiophene) in NH$_3$ is similar to that of the oxidized form in CH$_3$CN. Further studies of poly(3-methylthiophene) and derivatives shown to be durable upon reduction will be reported subsequently.


Use of Tris(trimethylsilyl)arsine To Prepare Gallium Arsenide and Indium Arsenide

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One of the processes commonly used for the epitaxial growth of GaAs and other compound semiconductors is organometallic chemical vapor deposition (OMCVD).[1] For GaAs, it has been the general practice to utilize a trialkylgallium compound and AsH$_3$ in this process, as exemplified by eq 1. However, concerns regarding the use

$$\text{Me}_3\text{Ga} + \text{AsH}_3 \xrightarrow[\sim 700\ °\text{C}]{\text{H}_2} \text{GaAs} + 3\text{MeH} \qquad (1)$$
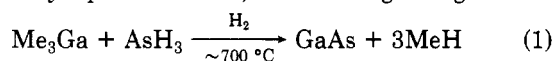
of AsH$_3$ have prompted a number of researchers to evaluate other sources of arsenic; thus, replacements for AsH$_3$ that have been studied include As, Me$_3$As, Et$_3$As, Et$_2$AsH, and t-BuAsH$_2$.[2] Alternatively, some adducts of gallium and arsenic compounds,[3–5] as well as a monomeric and a dimeric mono(arsino)gallane,[6,7] have been used as single-source GaAs precursors.

Recent research in our laboratories has demonstrated that dehalosilylation reactions (e.g., eq 2) are a facile route

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