Soluble polyacetylenes derived from the ring-opening metathesis polymerization of substituted cyclooctatetraenes: electrochemical characterization and Schottky barrier devices

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Invited Paper

Soluble polyacetylenes derived from the ring-opening metathesis polymerization (ROMP) of substituted cyclooctatetraenes: electrochemical characterization and Schottky barrier devices

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ABSTRACT

Recent developments in ring-opening metathesis polymerization (ROMP) have enabled the synthesis of poly-cyclooctatetraene (poly-COT), a material which is isostructural to polyacetylene. This liquid-phase polymerization method allows facile construction of interfaces, films, and devices with polyacetylene-like materials. The ROMP method also allows the preparation of soluble, yet highly conjugated polyacetylene analogs from substituted cyclooctatetraenes (R-COT). The redox characteristics of R-COT polymers were investigated at electrodes modified with thin polymer films. Voltammetric methods were used to characterize the redox response, band gap, electrochemical doping, and cis-trans isomerization properties of these polyenes. We have applied poly-COT technology to the fabrication of Schottky diodes and photoelectrochemical cells, by forming poly-COT films on semiconductor surfaces. The resultant semiconductor/organic-metal interfaces behave more ideally than semiconductor contacts with conventional metals, in that changes in the work function of the conducting polymer exert a large and predictable effect on the electrical properties of the resulting Schottky diodes. Transparent films of the solution-processible polymer poly-trimethylsilyl-cyclooctatetraene (poly-TMS-COT) have been cast onto n-silicon substrates and doped with iodine to form surface barrier solar cells. These devices produce photovoltages that are much larger than can be obtained from n-silicon contacts with conventional metals.

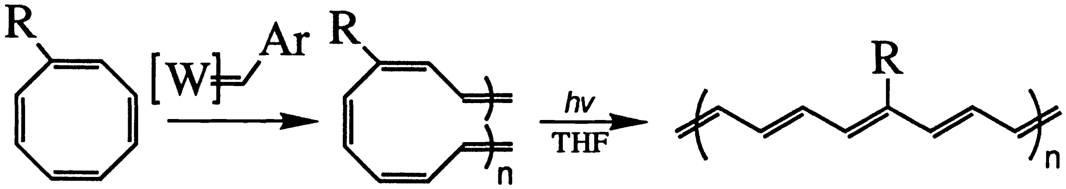
1. INTRODUCTION

Within the last 15 years, a large volume of work[1] exploring the synthesis and properties of polyacetylene has generated tremendous interest within the scientific community. As a one-dimensional semiconductor capable of either n- or p-type doping to high metallic conductivities, polyacetylene is a material with many potential applications[2] in diverse fields such as sensors, solar energy conversion, and lightweight batteries. However, the use of polyacetylene in many of these applications is hindered by an inherent lack of processability that is found in nearly all highly conjugated, and necessarily rigid, organic conducting polymers. Polyacetylene is a brittle, insoluble, and unprocessable material, classically formed by the exposure of acetylene gas to catalyst-treated surfaces. The polymer films which result have a fibrillar morphology and are semi-crystalline. Both the lack of processability of this material and its method of synthesis have hindered many potential applications where uniformly thin, mechanically strong films are required for casting onto a variety of substrates.

Considerable effort has been directed toward the preparation of soluble prepolymers from which polyacetylene may be obtained after processing.[3]

The synthesis of polyacetylene from the transition-metal catalyzed ring-opening metathesis polymerization (ROMP) of cyclooctatetraene, reported by Grubbs in 1988,[4] represents a liquid-phase route to polyacetylene. The resulting polymer, poly-cyclooctatetraene (poly-COT), has many of the same properties as polyacetylene formed by the classical (Shirakawa) polymerization of acetylene over Ziegler-Natta type catalysts. However, the liquid-phase ROMP method of synthesis is more amenable to the preparation of thin films and the fabrication of devices. More importantly, this method can be generalized to the polymerization of substituted cyclooctatetraenes.[5-7] Polymers from substituted cyclooctatetraenes (poly-R-COT), bear a substituent group every eight carbons on the average. Thus, the ROMP procedure provides substituted polyacetylenes not accessable from other monomers. It has been found that the appropriate choice of substituent results in a polymer which is soluble in common organic solvents (tetrahydrofuran, CH_2Cl_2) while retaining the high conjugation length required for doping to the metallic state.

As prepared, COT polymers have a high content of cis double bonds. In the case of the soluble poly-R-COT materials, a photochemical means of cis-trans isomerization has been developed,[5] which results in a mostly trans polyene. This serves as an alternative to the thermal isomerization method commonly employed for insoluble polyacetylene films (see Scheme 1).



Scheme 1. Synthesis of *trans*-poly-RCOT from a substituted cyclooctatetraene.

In this report, we describe the electrochemical characterization of poly-R-COT materials, demonstrating the ease with which surfaces (such as electrodes) can be modified. As a potential application of this technology, we also describe the properties of Schottky barrier diodes formed by the interface between n-silicon and a metallically doped coating of poly-COT. Further, we describe Schottky barrier solar cells formed from thin transparent layers of poly-trimethylsilyl-COT deposited from solvent onto n-silicon. We have previously reported on the unique features of these semiconductor/organic-metal interfaces and found them to be superior to traditional semiconductor/inorganic-metal devices.

Substituted cyclooctatetraenes were polymerized as previously described[5] by mixing the liquid monomer with the tungsten carbene catalyst:[8] $W(CHAr')(NAr)[OCMe(CF_3)_2]_2(THF)$ where $Ar = C_6H_5$ and $Ar' = o\text{-}MeOC_6H_4$. The polymer films were prepared and manipulated in a nitrogen filled dry-box. All electrochemical experiments were performed in the dry-box. All single-crystal silicon samples were ohmically contacted with gallium-indium eutectic, mounted in epoxy to cover the back contact and edges, and etched with 48% hydrofluoric acid before deposition of the polymer. n-Si samples were oriented along the (100) plane, and the p-Si samples were oriented in the (111) plane.

2. VOLTAMMETRIC STUDIES OF R-COT POLYMERS

2.1 Cyclic voltammetry and redox potentials

We have reported that, like polyacetylene, poly-R-COT films can be doped p-type with iodine vapour, or n-type with a tetrahydrofuran solution of potassium benzophenone. These redox processes have now been studied electrochemically. Voltammetry experiments were performed using carbon electrodes modified with thin (<0.2 μm) films of R-COT polymers. Using a microliter syringe, a small amount (0.5-3.0 μl) of a tetrahydrofuran polymer solution (0.3 mg/ml) was placed on the surface of a glassy carbon electrode, and the solvent was evaporated. Voltammetry was performed using a standard three-electrode configuration in a single compartment cell. The polymer modified electrode was placed in a voltammetry cell along with a platinum counter electrode and a Ag/Ag^+ reference electrode. The solvent/supporting-electrolyte was acetonitrile/0.1M $TBABF_4$ (tetra-*n*-butylammonium tetraflluoroborate). Though soluble in nonpolar solvents such as tetrahydrofuran, dichloromethane and toluene, the R-COT polymers were found to be insoluble in more polar solvents such as acetonitrile. The voltammograms obtained show reversible couples for both anodic and cathodic redox processes (see Figure 1). The anodic couple was characterized by sharp peaks with small peak separation (<100 mV). The cathodic couple generally shows slightly broader waves and a peak shape which is more dependent on scan rate and film thickness. The small voltammetric peak separations seen for these materials may be attributed to their amorphous morphology. Solvent cast films of R-COT polymers have been shown by microscopy[7b] to be unusually smooth in contrast to the fibrillar or pitted morphology frequently found for conducting polymers. Table 1 lists the oxidation and reduction potentials for a series of R-COT polymers. Also listed is the energy difference between the oxidation and reduction couples. Although this is not a rigorous measure of the band gap, these two values can be expected to show similar behavior.

The data of Table 1 reveal some interesting trends. Particularly noteworthy is the effect of substitution on oxidation potential. Relative to alkyl-substitution, the trimethylsilyl (TMS) polymer is more difficult to oxidize by 130 mV, and the *tert*-butoxy polymer is more easily oxidized by 130 mV. The TMS group is known as a π-acceptor,[9] while the *tert*-butoxy group is an electron donating substituent. There is also an observable effect of steric bulk on conjugation length. Within the series of butyl substituted polymers, *n*-butyl shows the smallest voltammetric "band-gap", while the bulky *tert*-butyl substituted polymer is so severely twisted that it cannot be doped anodically or cathodically within the available electrochemical window. This finding is supported by spectroscopic measurements in THF solution, where increasing conjugation length is indicated by a lower energy π-π^* transition.

The inability to measure the relative amounts of capacitive and faradaic charge in the electrochemical doping of a polymer film complicates the coulombic determination of stoichiometry.[10] With this point in mind, coulometric analysis of the electrochemical doping was attempted. In this experiment, a polymer modified electrode was swept through its anodic or cathodic couple within limits that closely bracketed the peak region of the voltammetric wave. This portion of the wave should represent predominantly faradaic charging. The charge passed was measured for the anodic sweep of the oxidation couple (p-doping), and the cathodic sweep of the reduction couple (n-doping). This measurement was carried out on the second cycle in order to avoid a "break-in" capacitance usually seen in the first cycle. The background charge passed in cycling the clean electrode was measured and subtracted.

For poly-*sec*-butyl-COT, oxidative doping from 0 to +0.4 V (all potentials are vs SCE) required 0.16 coul/mg, and reduction from -1.3 to -1.8 V required 0.16 coul/mg. These data imply stoichiometries of: (*sec*-butyl-COT)$_{3.76}$[BF$_4$] and (*sec*-butyl-COT)$_{3.76}$[TBA], or a chain-carbon/dopant molar ratio [(CH)X$_y$] of y=0.03. This result is dependent on potential and assumes no redox induced decomposition or capacitive charging. Under these conditions, a conjugation length of 3.76 COT units per soliton, or a soliton length of 30 carbon atoms is suggested as an upper limit.

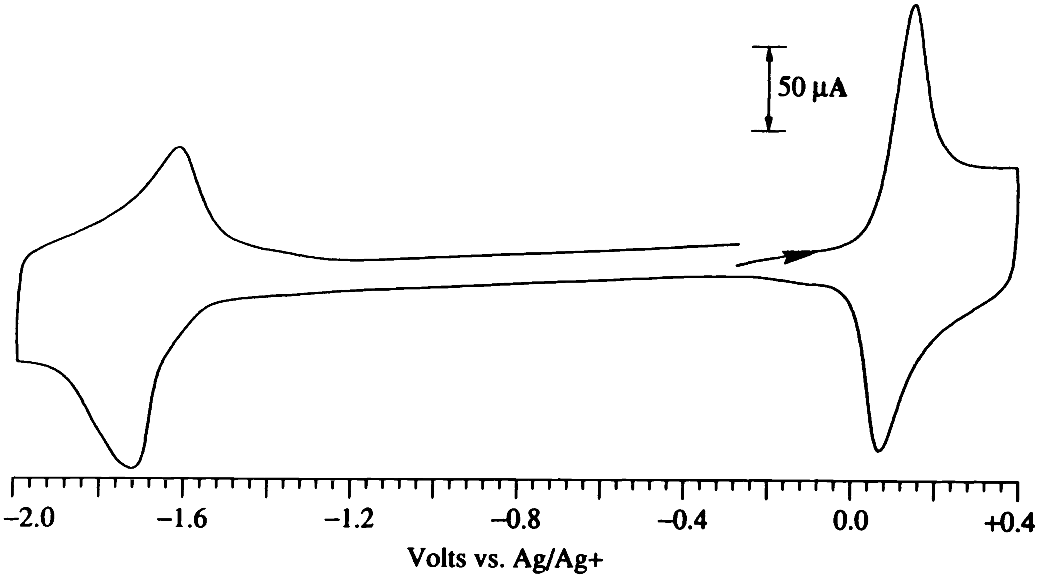


Figure 1. Representative cyclic voltammogram of *trans*-poly-*sec*-butyl-COT thin (<0.5 μm) film at a glassy carbon electrode, acetonitrile/0.1M TBABF$_4$, 50 mV/sec. Arrowhead indicates scan direction.

R	$E^{o\prime}_{red}$ (V)	$E^{o\prime}_{ox}$ (V)	$E^{o\prime}_{ox}$-$E^{o\prime}_{red}$(V)	λ_{max}(nm)[a]
tert-butyl	- - -[c]	- - -[c]	- - -[c]	432
TMS	-1.44	+0.37	1.81	538
sec-butyl	-1.55	+0.25	1.80	556
n-butyl	-1.54	+0.23	1.77	- - -[b]
tert-butoxy	-1.49	+0.10	1.59	595

Table 1. Voltammetric potentials vs. SCE taken as (E_p^a+E_p^c)/2. (a) spectra measured in dilute THF solution. (b) trans polymer is insoluble. (c) cannot be doped between -2.5V and +2.8V

2.2 Electrochemical Cis-Trans Isomerization

The voltammetry described above was performed with photochemically isomerized trans polymers. When the same voltammetric experiments were performed with the cis polymer, the voltammograms shown in Figure 2 were obtained. In both anodic and cathodic processes, the cis polymer gave a voltammetric wave at more extreme potentials than those seen for the trans polymer. This wave was seen only on the first cycle. Subsequent cycles are identical to those of the trans polymer. Thus, the voltammetry suggests an electrochemical cis-trans isomerization process. The wave seen in the first cycle represents oxidation or reduction of the cis polymer (appropriately at more extreme potential values). This redox reaction, or doping results in isomerization of the polyene chain to the more thermodynamically stable trans geometry. It is known that isomerization accompanies the chemical doping of high-cis polyacetylene.[11] More recently, there have been reports of cis-trans isomerization concurrent with electrochemical doping.[12] Our observations with poly-R-COT materials are in congruence with these findings.

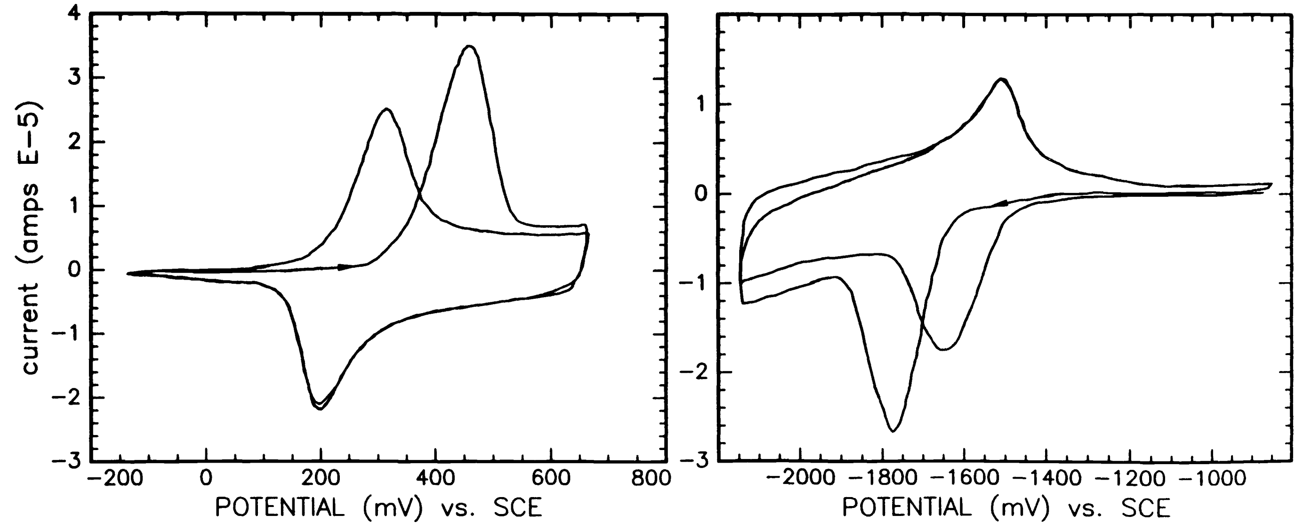


Figure 2. Cyclic voltammograms of *cis*-poly-*sec*-butyl-COT thin (<0.5 μm) films at a glassy carbon electrode, acetonitrile/0.1M $TBABF_4$, 50 mV/sec. Arrowheads indicate scan direction of first cycle. **Top**: Anodic isomerization **Bottom**: Cathodic isomerization.

To show that the voltammetric behavior indeed indicates isomerization, transparent electrodes were employed and the visible spectrum was monitored before and after cycling through the anodic or cathodic redox couple. A cis-polymer solution was spin coated onto an indium tin-oxide transparent glass electrode, providing a homogeneous thin polymer film. The transparent electrode was inserted into a two-compartment electrochemical cell containing acetonitrile/0.1M $TBABF_4$. After potentiostatic cycling through either the anodic or cathodic couple, the transparent electrode was removed from the cell and washed in clean acetonitrile. It was then fitted into an anaerobic chamber, removed from the dry-box and the visible absorption spectrum was measured. In the case of poly-TMS-COT, the cis film showed λ_{max}= 380 nm prior to electrochemistry and λ_{max}= 530 nm after a single anodic cycle (-0.4 to +0.8V at 20 mV/sec). The same spectrum was obtained after a single cathodic cycle (-0.4 to -1.9V at 20 mV/sec) of another cis film. In the case of poly-*sec*-butyl-COT, the familiar visible spectrum of the cis polymer (λ_{max}= 352 nm) was changed to that of the trans polymer (λ_{max}= 540 nm) after a single anodic (-0.4 to +0.8 V at 20 mV/sec) or cathodic (-0.4 to -2.0 V at 20 mV/sec) cycle.

The anodic isomerization process for *cis*-poly-TMS-COT and *cis*-poly-*sec*-butyl-COT was investigated by coulometry. It was determined that the amount of charge passed in the first anodic sweep, which results in isomerization, is nearly the same as the charged passed on the next anodic sweep between the same limits. This indicates that the amount of charge required for doping and isomerization of a cis polymer film is nearly equivalent to the charge required for doping of the resulting trans film. Further, it was found that when the cis wave was swept only partially, the amount of charge passed in the very next cycle indicated only partial isomerization. Specifically for poly-*sec*-butyl-COT on glassy carbon, if the cis wave is completely swept from 0 to +0.60 V on the first cycle (50 mV/sec), full isomerization is seen. The second anodic sweep shows a trans oxidation wave with a peak potential at +0.28 V. If this sweep is continued to +0.60 V, the anodic charge passed is nearly equivalent to that passed in the isomerization sweep (anodic$_1$/anodic$_2$ = 1.08). If the isomerization sweep is reversed at +0.40 V, only 17% of the full isomerization charge is passed, and the next anodic sweep shows a trans

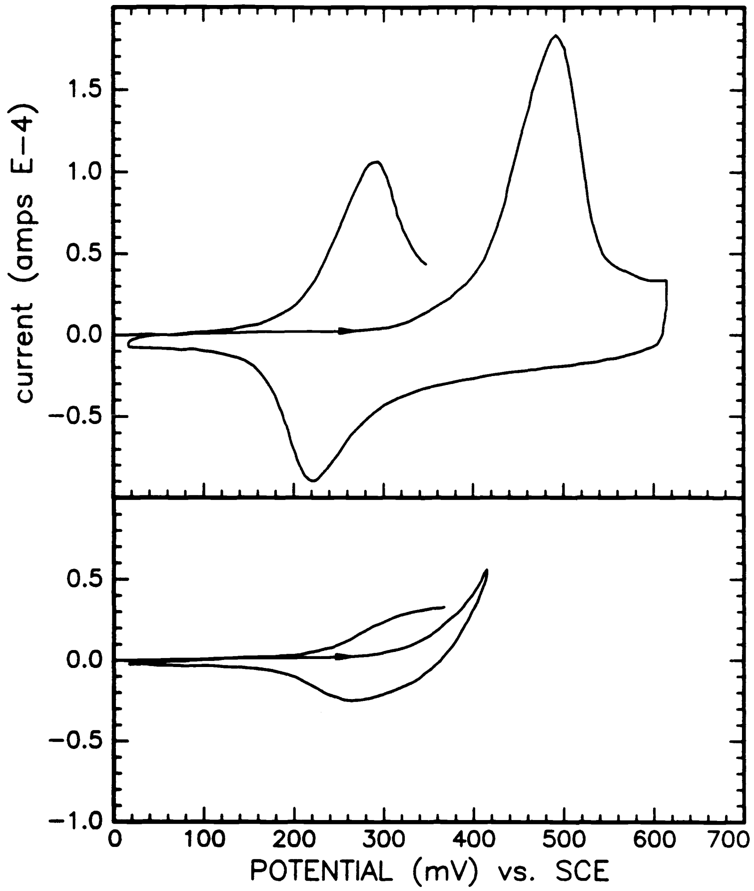


Figure 3. Full anodic isomerization requires full doping. **Top:** cyclic voltammogram of *cis*-poly-*sec*-butyl-COT thin film at a glassy carbon electrode, acetonitrile/0.1M TBABF$_4$, 50 mV/sec. First scan indicates redox of cis polymer with accompanying isomerization. **Bottom:** partial isomerization (see text).

oxidation wave which passes only 23% of the charge expected for a fully isomerized polymer film cycled between those limits (see Figure 3). This result indicates that the electrochemical isomerization is not electrocatalytic and that incomplete doping of a cis film results in incomplete isomerization.

3. SCHOTTKY BARRIER DIODES AND SOLAR CELLS

3.1 Basic concepts

The operation of a Schottky diode is based on thermionic emission of majority-carriers (electrons for n-type, holes for p-type) over an electrostatic barrier that forms at the metal/semiconductor interface. The size of the barrier determines the rate of charge transport across the interface, and thus the rectification properties of the resulting diode are controlled by the barrier height. The barrier height, Φ_b, for thermionic emission is related to the reverse saturation current density, J_o, by

$$J_o = A^{**}T^2\exp(-q\Phi_b/kT) \tag{1}$$

where Φ_b is the barrier height, k the Boltzmann constant, T the temperature in K, q the electronic charge, J_o the limiting reverse bias (exchange) current density, and A^{**} is the modified Richardson constant. The current density-voltage properties are then determined by

$$J = J_o(\exp(qV/AkT) - 1) \tag{2}$$

where A is the diode quality factor, equal to 1 for the thermionic emission mechanism. In an ideal system, Φ_b is determined by the relative potential energies (Fermi levels) of the mobile charge carriers in the semiconductor and contacting phases. Hence the barrier height of a Schottky diode should be directly related to the work function of the metal contact. A long standing problem associated with Si, GaAs, and InP has been that the barrier heights of the semiconductor/metal contacts are not controlled by the work function in the metal. Rather, the Fermi levels of Si, GaAs, and InP contacts are "pinned" at specific energies. The rectification characteristics of the resulting diodes therefore are not sensitive to the work function of the metal used. This pinning of Schottky barrier height also limits the performance of Schottky photocells. For Schottky photocells, the light absorbed within the semiconductor produces electron-hole pairs which can be separated by the electric field formed by contact with the metal overlayer. The larger the barrier height, the more efficient will be this process of electron-hole separation. Thus the same factors that leads to highly rectifying Schottky barriers will give rise to more efficient Schottky solar cells.

3.2 Dark characteristics of n-Si/poly-COT(I_2 doped) cells

We have previously reported that the rectification characteristics for metallically doped polyacetylene contacts to silicon *are* sensitive to the work function of the organic metal phase, in contrast to the situation encountered with conventional metals.[6] Metallicaly dopoed polyacetylene is unique in that its work function may be varied depending on the type of doping used. Iodine or p-type doping gives a high work function organic metal, and potassium or n-type dopants produce a low work function organic metal. A thick layer of poly COT can be easily formed on a silicon electrode by placing several drops of the monomer/catalyst solution on the silicon surface before complete reaction results in a dry film. These devices were not suitable for photocurrent studies due to the thickness of the polymer overlayer. However, after doping, diodes were formed which were characterized by their current vs. potential curves. It was found that n-silicon forms a rectifying contact with iodine doped poly-COT ($J_o = 10^{-8}$ A cm^{-2}), and an ohmic contact with potassium doped poly-COT. p-Silicon forms a highly rectifying contact with potassium doped poly-COT ($J_o = 10^{-7}$ A cm^{-2}), and a poorly rectifying contact with iodine doped poly-COT ($J_o = 10^{-3}$ A cm^{-2}). The diode quality factors, A, all lie between 1.2 and 1.8. For highly doped polyacetylene contacts to conventional semiconductors, the mechanism of charge transport is usually assumed to be thermionic emission, which is the transport mechanism operative in semiconductor/metal Schottky diodes. The observation of diode quality factors greater than 1 is a general one for semiconductor/conducting polymer interfaces, and it indicates that the simple thermionic emission mechanism that controls conventional Schottky diodes is inadequate to describe these junctions (thermionic emission theory requires a quality factor of 1). A variety of factors, such as carrier recombination in the depletion region of the semiconductor or a bias-dependant barrier height, can lead to ideality factors greater than unity and might play a role in the dark conduction mechanism of these devices.

3.3 Photocurrent measurements for n-silicon/poly-TMS-COT(I_2 doped) solar cells

When Schottky solar cells are illuminated, they produce a photocurrent, J_{ph}, which can be considered to modify the diode equation (eq. 2) according to eq. (3)

$$J = J_o(\exp(qV/AkT) - 1) - J_{ph} \tag{3}$$

At open circuit, J = 0 and V = V_{oc}, the open-circuit voltage. Thus eq. (3) can be rearranged to give the relationship between J_{ph} and V_{oc} (for $V_{oc} > 3kT$).

$$\ln(J_{ph}) = qV_{oc}/AkT - \ln(J_o) \tag{4}$$

Thin films of poly-TMS-COT were formed on epoxy mounted silicon electrodes by deposition from tetrahydrofuran solution. The polymer solution was first photo-isomerized to the more stable trans isomer. Electrical contact was made to the polymer overlayer by a gold wire. The device was then doped p-type, by iodine vapor in an evacuated chamber. A plot of $\ln(J_{ph})$ vs V_{oc} for the n-Si/poly-TMS-COT(I_2 doped) contact is shown in Figure 4. At high light intensities ($V_{oc} > 500$ mV), the slope of this curve yields a diode quality factor of close to 1 and a value for J_o of 10^{-13}. This value of J_o is much smaller than can be obtained with conventional Schottky devices, and is very close to the lower limit set by carrier recombination in the neutral region of the silicon crystal. The lower limit imposed on J_o, based on this bulk diffusion/recombination process, is given by eq. (5):

$$J_o = qD_p n_i^2/L_p N_D \tag{5}$$

where D_p is the hole diffusion coefficient, n_i is the intrinsic carrier concentration, N_D is the number density of dopant atoms, and L_p is the hole diffusion length for the particular sample of silicon used. Using equations (4) and (5), and the restriction that A = 1 for the bulk recombination/diffusion mechanism, an upper limit on the value of V_{oc} can be calculated for given values of N_D and L_p (eq. 6).

$$V_{oc} = (kT/q)\ln(L_pN_DJ_{ph}/qD_pn_i^2) \tag{6}$$

Table 2 lists the predicted V_{oc} values along with the open circuit voltages obtained on a series of n-Si/poly-TMS-COT (I_2 doped) cells constructed from silicon samples of different resistivities (dopant densities) and diffusion lengths. At high light intensities (ca. 20 mA cm^{-2} current density), the polymer based cells all reached the bulk recombination limit. The open circuit voltage data and plots of V_{oc} vs. log (J_{ph}) indicate that bulk diffusion/recombination is the limiting recombination mechanism in these devices at the higher light intensities. This contrasts with conventional silicon/metal junctions, which are controlled by the thermionic emission mechanism previously described. Interfacial Fermi level pinning limits the barrier heights in the Si/metal systems and consequently the maximum values of the open circuit voltages are limited to 200-300 mV (at 20 mA cm^{-2} current density). At low light intensities, the values of J_o and A extracted from the log (J_{ph}) vs V_{oc} plot were the same as for the dark current density-voltage curve, which both indicate that the limiting exchange current density, $J_o=10^{-8}$ A cm^{-2}, and the diode quality factor is 1.4. The cell performance in the dark is similar to that described above for silicon/poly-COT diodes, and indicates that a conduction mechanism different from bulk recombination dominates at lower current densities for these interfaces.

The unoptimized n-Si/poly-TMS-COT(I_2 doped) devices showed overall solar conversion efficiencies of between 1 and 5% under high (80-100 mW/cm^2) light intensities, with the main sources of efficiency loss being series and parallel (shunting) resistances (electrical contacts to the polymer were made with gold wires or transparent indium tin oxide-coated glass slides; typically Rs = 100 Ω and Rp = 10^5 Ω for the ITO contacts). The efficiencies also were not corrected for reflection or absorption losses which could be minimized to increase the incident-light based quantum yield (the ca. 200 Å thick poly-TMS-COT(I_2 doped) layer transmits between 89-94% of the light in the visible region).

3.4 Comparison to Si-liquid junctions

In silicon/liquid-junction cells the rectification properties are determined by the redox species present in solution. Highly rectifying (large barrier) to totally ohmic (barrierless) junctions can be obtained simply by changing the redox couple in solution. Thus, similar to the silicon/polymer cells described here, liquid junction cells are not subject to the same Fermi level pinning constraints as the silicon/metal analogs. Another similarity is that the silicon/methanol junction cells have been shown to be limited by the bulk recombination mechanism at high light intensities. Doped polyacetylene is an electronic conductor, although, like electrolytic solutions, it possesses a lower concentration of acceptor states than conventional metals. Saturation doping of polyacetylene with iodine results in roughly 10^{21} cm^{-3} of positive soliton states (the states responsible for conduction in oxidatively doped polyacetylene), while in a liquid 1 Molar in redox species, the

n-Silicon Resistivity (Ω-cm)	Lp (μm)	Voc (Theory) (V)	Voc (Si/polymer) (V)	Voc (Si/Au) (V)
0.245	315	0.64	0.64	0.30
1.0	337	0.59	0.59	0.28
1.59	13	0.50	0.49	0.30
3.54	382	0.56	0.57	0.29
12.4	387	0.53	0.53	0.30

Table 2. Open circuit voltages, at 20 mA/cm^2 short circuit current density and 296K, for n-Si/ poly-TMSCOT (iodine doped) and n-Si/ Au solar cells. V_{oc} (Theory) is the maximum possible, calculated from equation *4*. Diffusion lengths were measured by spectral response.

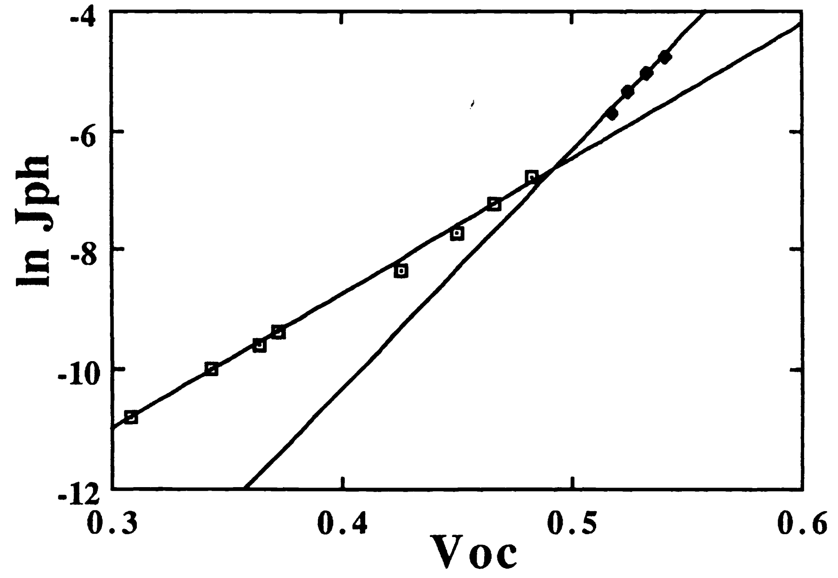


Figure 4. Plot of J_{ph} vs. V_{oc} for the solar cell n-Si/poly-TMSCOT (iodine doped). Data points at high V_{oc} give A = 1.0 and $J_o = 10^{-13}$ A cm^{-2}. Data at lower light intensity give A = 1.7 and $J_o = 10^{-8}$.

density of acceptor states is on the order of 10^{20} cm^{-3}. By contrast, in metals the density of acceptor states at the Fermi energy is typically 10^{23} cm^{-3}.

The interfacial chemistry may also contribute to the similarities seen between liquid and polymer junctions. The formation of an interface by casting a polymer film at room temperature is inherently a lower energy process than metal deposition from a hot filament, and the interface that results from the two techniques can be expected to be quite different. Thus it is possible that deleterious effects such as the formation of interfacial trap states is not as prevalent in the polymer system as in the semiconductor/metal system. Similar improvements in electrical characteristics have been found for electrodeposited metal films.

6. CONCLUSION

ROMP of substituted cyclooctatetraenes provide a new class of soluble conducting polymers. Films can be easily cast from solution onto electrodes or other substrates. Preliminary electrochemical results indicate that the substituent group not only imparts solubility to the polymer, but allows electronic and steric perturbations to directly effect redox potentials and band gap. These studies also show an electrochemical cis-trans isomerization for *cis*-poly-R-COT materials analogous to that reported for *cis*-polyacetylene. At present, new R-COT polymers are under investigation in which the substituent offers strong electronic perturbation to the conjugated polymer, or is itself electroactive. Current interest also centers on the electrodeposition of thick free-standing films, and the fabrication of multi-layered films from the sequential electrodeposition of several different R-COT polymers.

In silicon/polyacetylene contacts, we have demonstrated that the rectification behavior can be manipulated in a predictable fashion by changing the dopant in the polymer. Silicon contacts can be made with polyacetylene that are much more rectifying than any metal Schottky contacts, indicating that the polymer systems are not subject to the same Fermi level pinning constraints as conventional metal contacts. Thin films of the soluble polyacetylene analog poly-TMSCOT can be cast onto n-silicon substrates and doped with iodine to form solar cells. Although the limiting conduction mechanism of metal/silicon contacts is thermionic emission of electrons over the Schottky barrier, the mechanism limiting the silicon/poly-TMS-COT(I_2 doped) interface is clearly a bulk diffusion/recombination mechanism at high illumination intensities. The conduction mechanism in the dark is not known, although the evidence presented here indicates that it cannot be simple thermionic emission.

7. ACKNOWLEDGEMENTS

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