

Interaction of Oxygen with Conjugated Polymers: Charge Transfer Complex Formation with Poly(3-alkylthiophenes)

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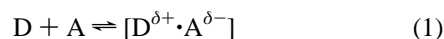
Abstract: Molecular oxygen forms a reversible charge transfer complex (CTC) with poly(3-alkylthiophenes). The complex is weakly bound but possesses a distinct absorption band in the visible region. The electronic properties of the neutral polymer are modulated by the CTC. The extent of modulation of these properties is proportional to oxygen pressure and is fully reversible. Analysis of poly(3-hexylthiophene) field effect transistors under increasing pressures of oxygen shows that the carrier concentration increases, conductivity increases, and the charge carrier mobility is lowered by the formation of the charge transfer complex. The CTC manifests itself as a fluorescence quencher of mobile polaronic excitons, and it explains why oxygen quenches luminescence with much greater efficiency than predicted by a collisional quenching model. Implications of the charge transfer complex on the photochemistry of poly(3-alkylthiophenes) and photosensitization of singlet oxygen are discussed.

Introduction

π -Conjugated polymers have received considerable attention because of their high conductivity in the partially oxidized form, and because of their semiconducting and luminescence properties in the neutral form. Of this class of polymer, the polythiophenes have been intensively studied due to their favorable processability and relative stability.¹ Furthermore, the “band gap energy” of the polymer can be tuned at the molecular level by introduction of sterically-hindered sites or by derivatization with electron-withdrawing or electron-donating substituents.^{1d,2} By chemical modification of the polymers, the wavelength and efficiency of photoluminescence and electroluminescence can be tuned. Quantum yields of photoluminescence are relatively low for these materials, particularly in the solid state, due to a combination of inter- and intramolecular nonradiative decay mechanisms.³ In addition, the material's field effect conductivity has provided an impetus for studying polymer-based field effect transistors. The polymers exhibit hole mobilities typically in the order of 10^{-4} – 10^{-5} cm² V⁻¹

s⁻¹.⁴ Much higher mobilities have been measured for carefully controlled samples and oligomers.⁵ In studies of luminescence and electronic properties ambiguities exist which point to a specific interaction between oxygen and the polymer.⁶ For example, oxygen quenches fluorescence with greater efficiency than predicted by collisional quenching alone, and studies of electronic properties generally indicate an increase in conductivity of polythiophene films in the presence of oxygen.

It is well-known that association of a molecule of low ionization potential (an electron donor, D) with a molecule of relatively high electron affinity (an electron acceptor, A) can lead to a weakly bound donor–acceptor complex or charge transfer complex (CTC) (eq 1).⁷ Upon association, the physical properties of the donor and acceptor are perturbed and new properties arise.



In order to explain some of the phenomena observed in polythiophenes and conjugated polymers in general, we investigated the existence of a charge transfer complex (CTC) between poly(3-hexylthiophene) and O₂. The complex is studied by using absorption, luminescence, electron paramagnetic resonance spectroscopies, and field effect conductivity.

Experimental Section

Polymer Synthesis and Purification. Polymerization of 3-hexylthiophene was achieved by chemical oxidative coupling.⁸ The solid product was filtered and washed successively with ammonia solution

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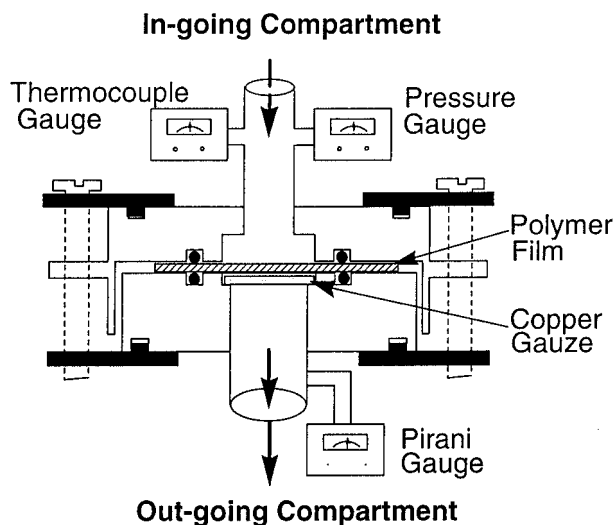


Figure 1. Schematic diagram of the time-lag diffusion cell.

(28%), water, and acidified methanol. The crude polymer was dissolved in hot dichloromethane, and insoluble products were removed by filtration. The precipitate was filtered and dried under reduced pressure at 50 °C. The sample was purified further by soxhlet extraction with methanol (2 days) and acetone (5 days). The polymer was purified further by treating a solution of the polymer in CHCl_3 with ammonia solution (28%). The number average molecular weight of the polymer, M_n , was 8500, and the molecular weight distribution (MWD) was ~ 3 . The ratio of head-to-tail:head-to-head dyads was 80:20 as determined by ^1H NMR. λ_{max} was 435 nm for polymer solutions (CHCl_3) and 518 nm for polymer films. The iron content was determined by standard acid digestion procedures followed by atomic absorption spectroscopy.⁹ The polymer contained 0.05 wt % (0.15 mol %) iron impurities.

UV-vis Spectroscopy and Luminescence Studies. UV-vis spectra were recorded on a Cary E1 spectrophotometer at 25 °C. Steady state luminescence was measured on a LS-100 spectrofluorometer (Photon Technology International Inc.). Polymer films ($\sim 20 \mu\text{m}$) were cast onto quartz substrates from CHCl_3 solutions. Oxygen-free films were obtained from degassed polymer solutions (freeze-pump-thaw method) by casting under an oxygen-free N_2 atmosphere. For UV-vis absorption measurements the films were enclosed in an air-tight stainless steel cell and vacuum pumped for several days to remove residual oxygen. For luminescence studies, oxygen-free films were placed in a quartz cell under oxygen-free N_2 and vacuum pumped for several days. The effect of oxygen was studied by introducing oxygen under controlled pressure. The optical density of polymer solutions was < 0.1 at their absorption maxima. Quantum yields of fluorescence were determined by using 9,10-diphenylanthracene [$\phi_{\text{fl}}(\text{hexane}) = 0.54$] and rhodamine B [$\phi_{\text{fl}}(\text{ethanol}) = 0.69$] as standards.¹⁰ For determining quantum yields of thin films, 9,10-diphenylanthracene ($< 10^{-3} \text{ M}$) in poly(methyl methacrylate) ($\phi_{\text{fl}} = 0.83$) was used as standard. Quantum yields of films are quoted *in vacuo*, while solutions were purged with O_2 -free nitrogen.

Solubility of Oxygen. The apparatus employed for the determination of oxygen permeability and concentration is illustrated in Figure 1. The diffusion cell is composed of ingoing and outgoing compartments. Free-standing polymer films ($\sim 30\text{-}\mu\text{m}$ thick) were supported by a fine copper gauze. The two halves of the assembly were sealed between Teflon rings. The pressure of the low- and high-pressure compartments was measured by various pressure gauges to an accuracy of 1% of decade. Oxygen was introduced into one-half of the degassed cell at a pressure of 760 Torr. Permeation of the gas through the membrane was monitored by measuring the change in pressure in the outgoing compartment with time. At steady state, the amount of permeant passing through a polymer film, Q_t , is given by

$$Q_t = \frac{D_g c_1}{l} \left[t - \frac{l^2}{6D_g} \right] \quad (2)$$

where l is the film thickness, t is time, and c_1 is the permeant concentration where in the high pressure side of the membrane. D_g is the diffusion coefficient of the gas in the membrane. The solubility of gases in polymer films is assumed to follow Henry's law (eq 3)

$$c = S_g p_g \quad (3)$$

where c is the concentration of gas in the polymer film, p_g is the partial pressure of the gas at the gas-polymer interface, and S_g is the solubility coefficient. The relationship between S_g and the permeation coefficient, P , is given by

$$P = D_g S_g \quad (4)$$

so that eq 2 becomes

$$Q_t = \frac{P p_g}{l} \left[t - \frac{l^2}{6D_g} \right] \quad (5)$$

The linear portion of a plot of Q_t against time t is proportional to P , and through eqs 4 and 5, the concentration, while the intercept extrapolated to $t = 0$ provides the time lag θ (see Figure 4), defined by eq 6¹¹

$$\theta = \frac{l^2}{6D_g} \quad (6)$$

Fabrication of Devices. Silicon was chosen as the support substrate for the fabrication of polymer devices because it can be heavily doped to form a gate electrode and thermally oxidized to yield a silicon oxide insulating layer. The Si substrate plays no *active* role in the device operation. Two interdigitated structures of gold were deposited photolithographically on top of the insulator and used as source and drain. The polymer semiconductor layer was cast on the structure from degassed polymer solutions under oxygen-free N_2 and placed in an integrated circuit carrier sealed inside an air-tight compartment. Details of the procedure are given elsewhere.^{4e,6} Vacuum or oxygen were applied as required. Figure 2 shows a schematic diagram of the polymer-FET.

Current-voltage characteristics of polymer-FETs were measured with a semiconductor parameter analyzer HP4145 and a Bausch and Lomb wafer probing station. The drain-source current, I_{DS} , was measured as a function of the drain-source voltage, V_{DS} , to observe FET-like characteristics, while plots of I_{DS} versus gate-source voltage, V_{GS} , were constructed to determine the gate bias modulation of the FET conductive channel. The total current of a polymer-FET was separated into two components: channel current (I_{ch}) and bulk current (I_{bk}). With use of established metal-oxide-field effect transistor (MOSFET) current-voltage relationships, the channel current can be formulated as

$$I_{\text{ch}} = \mu C_{\text{ox}} \frac{W}{L} \left\{ (V_{\text{GS}} - V_{\text{T}}) V_{\text{DS}} - \frac{1}{2} V_{\text{DS}}^2 \right\} \quad (7)$$

for linear operation modes, where L and W are channel length and width, respectively; V_{T} is the threshold voltage; μ is the carrier mobility; and C_{ox} is the capacitance of the oxide layer. The bulk current can be represented as

$$I_{\text{bk}} = \sigma \frac{W}{L} V_{\text{DS}} \quad (8)$$

where l is the polymer layer thickness.

In our analysis of $I_{\text{DS}} - V_{\text{DS}}$ responses, three assumptions are made: (1) The current at zero gate bias is considered to be the Ohmic current that flows through polymer substrate. The channel current below the

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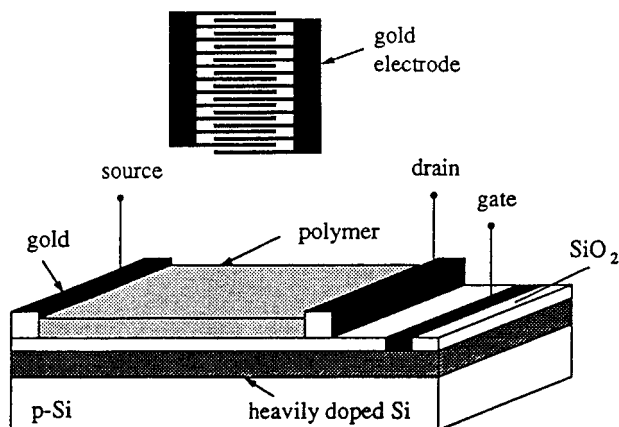


Figure 2. Schematic representation of the polymer-metal-insulator field effect transistor.

threshold voltage is negligible compared with the bulk region current. (2) Bulk current at positive gate biases is equal to that at zero gate bias. The accumulation layer thickness is comparatively much smaller than the polymer bulk thickness, therefore the bulk region thickness does not show a considerable change upon formation of an accumulation layer. (3) Mobility is considered only to be a weak function of gate bias, especially in the low-voltage range (0 to -30 V). Based on these above assumptions and equations, the bulk conductivity can be determined from $I_{DS} - V_{DS}$ at zero bias. The bulk current is subtracted from currents at negative biases to determine the FET-like channel currents. Mobilities are determined by using conventional MOS parameter extraction methods.

Results

UV-vis Spectroscopy. The energy associated with excitation of a charge transfer complex is given by

$$E_e = IP_D - EA_A - W \quad (9)$$

where IP_D and EA_A are the ionization potential of the donor and the electron affinity of the acceptor, respectively. W is the Coulombic attraction energy of the complex.¹² E_e can be estimated with reasonable accuracy with use of the following empirical relation:¹³

$$E_e(\text{eV}) = E_{1/2}^D - E_{1/2}^A + 0.15 (\pm 0.10) \quad (10)$$

$E_{1/2}^D$ and $E_{1/2}^A$ represent the half-wave electrochemical potentials of the donor and acceptor, respectively. The 0.10-eV error is a result of uncertainty in the solvation energy of the complex. The lowest energy for the P3HT- O_2 complex was estimated to be $\sim 1.9 \pm 0.1$ eV (648 ± 33 nm) by using measured $E_{1/2}$ values of -0.82 and ~ 0.94 vs SCE in $CH_3CN/TEAP$ for oxygen and poly(3-hexylthiophene), respectively.¹⁴

In order to detect this absorption, films of P3HT were subjected to variable pressures of oxygen and the visible spectrum recorded *in situ*. Films of P3HT possess a broad absorption spectrum with a maximum absorption at ~ 518 nm and an absorption tail that extends to 675 nm. The presence of oxygen was found to perturb the optical density of the absorption tail of P3HT. The difference spectra of the polymer in the presence and absence of oxygen shows a structureless band at ~ 630 nm (Figure 3). The proximity of this band to the predicted value for the CTC, as well as the fact that the absorbance was

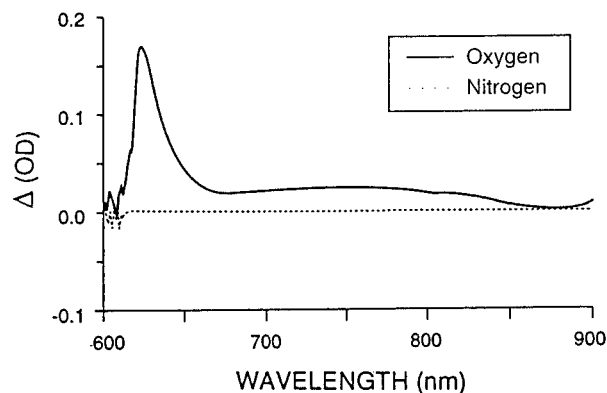


Figure 3. UV-vis absorption difference spectra of a P3HT thin film ($20 \mu\text{m}$) in contact with oxygen (10 atm) and under oxygen-free N_2 . Reference, O_2 -free film.

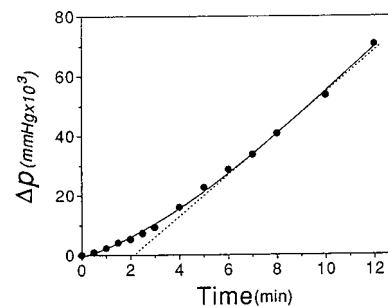


Figure 4. Pressure-time relationship for oxygen diffusing through a $30\text{-}\mu\text{m}$ film of P3HT under 760 mmHg oxygen pressure. Temperature is 298 K.

directly proportional to the pressure of oxygen within the range 0.0–10 atm, is strong evidence for a charge transfer complex between molecular oxygen and poly(3-hexylthiophene).

For a donor molecule in large excess with respect to the acceptor, the optical density of the CTC is related to the concentration of the acceptor and donor through the Benesi-Hildebrand relation.¹⁵ For a polymer film this can be written as

$$\frac{d[A]}{OD_{CTC}} = \frac{1}{\epsilon_{eff}} + \frac{1}{K_x \epsilon_{eff} x_D} \quad (11)$$

where d is the film thickness (i.e., the optical path length), x_D represents the mole fraction of donor, and $[A]$ is the concentration of the acceptor. OD_{CTC} and ϵ_{eff} are the optical density and the effective extinction coefficient of the complex. K_x is the equilibrium constant of the complex based on mole fractions of the constituent species. A Benesi-Hildebrand plot of $d[A]/OD_{CTC}$ versus $1/x_D$ should lead to estimates of ϵ_{eff} and K_x , but this first requires estimations of the donor and acceptor concentrations. The acceptor concentration, the dissolved oxygen concentration, in the polymer film was measured indirectly via the measurement of oxygen diffusion as described in the Experimental Section.

Solubility and Diffusion Coefficient of Oxygen. Figure 4 shows the pressure-time relationship for oxygen diffusing through a film of P3HT under 760 mmHg oxygen pressure. From the time lag, θ , the diffusion coefficient, D , was determined according to eq 6. The value for the diffusion of O_2 in P3HT films was estimated to be $1.2 \times 10^{-8} \text{ cm}^2 \cdot \text{s}^{-1}$. The slope of the linear portion provides a measure of the

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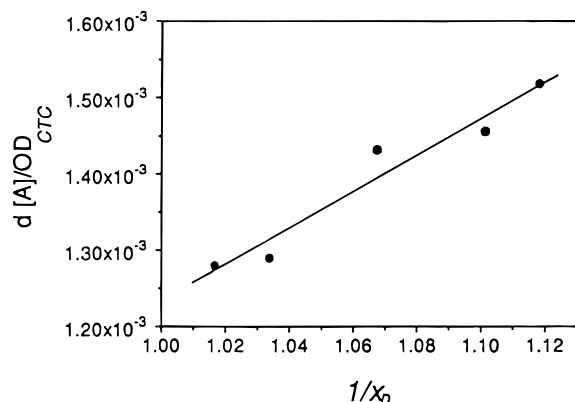


Figure 5. Benesi–Hildebrand plot for the P3HT·O₂ complex. The pressure of oxygen was varied from 0 to 10 atm.

permeation coefficient. The permeation coefficient, P , of O₂ in P3HT films was estimated to be $3.4 \times 10^{-11} \text{ cm}^2 \text{ s}^{-1}$. Accordingly, solubility of oxygen in P3ATs was determined to be 0.22 v/v at standard temperature and pressure (STP). This solubility coefficient was used to determine the concentration of oxygen in the polymer at various oxygen pressures according to eq 3.

Equilibrium Constant and Energetics. The concentration of the donor in the film, $[D]_{\text{film}}$, can only be estimated by considering the minimum number of conjugated thienyl rings required to form a detectable CTC. We postulate that the interaction of oxygen with long π -conjugation lengths will dominate over interactions with short conjugation lengths due to the lower ionization potential of the former. We note that the oligomer, α -sexithienyl, has a similar absorption maxima and thus a similar degree of conjugation to that of the polymer. If we tentatively assume the donor unit as being represented by a sexithienyl segment then $[D]_{\text{film}}$ is calculated to be 1.09 M (assuming a density of 1.1 g/cm³).¹⁶

Given these estimations of oxygen solubility and donor concentration, ϵ_{eff} and K_x are thus calculated to be $\sim 800 \text{ M}^{-1} \text{ cm}^{-1}$ and 0.72, respectively, from the linear Benesi–Hildebrand plot shown in Figure 5. It is noteworthy that the evaluation of K_x , unlike ϵ_{eff} , is independent of the concentration of dissolved oxygen used in the calculations.^{15b} K_x can be readily converted to a concentration-based constant, K_c , since in the absence of solvent, and where the donor is in large excess, $K_c = K_x \overline{V_D}$, where $\overline{V_D}$ (0.91 M⁻¹) is the molar volume of the donor, based on the sexithienyl segment. K_c was calculated to be 0.47 M⁻¹.

From the relationship

$$K_c = \frac{[\text{CTC}]}{([\text{D}] - [\text{CTC}])([\text{A}] - [\text{CTC}])} \quad (12)$$

the concentration of the CTC was calculated to be $\sim 1.3 \times 10^{-3} \text{ M}$ when films are exposed to ambient air.¹⁷ From this we conclude that $\sim 1\%$ of the π -conjugated segments and $\sim 30\%$ of solubilized oxygen molecules form a charge transfer complex upon exposure to air. The low equilibrium constant for charge transfer complex formation is indicative of a weak molecular complex. These have been coined by Mulliken as “contact charge transfer complexes” and arise from statistical collisions between donor and acceptor molecules.^{15b,18} In the present case,

the chance interaction of oxygen perturbs the π -conjugated segment of poly(3-hexylthiophene) to form a CTC. The intensity of the lowest energy transition of this complex is largely borrowed from the allowed singlet π - π^* of the polymer.

The energetics of CTC formation was estimated through determination of free energy change and binding energy of molecular association from $\Delta G^\circ = -RT \ln K$ and $\Delta G^\circ = \Delta H^\circ - T\Delta S^\circ$. The standard free energy change (ΔG°) for formation of P3HT·O₂ CTC was determined to be -1.9 kJ/mol at 298 K. CTC's typically exhibit ΔS° values in the range of -8 to $-14 \text{ cal deg}^{-1} \text{ mol}^{-1}$,¹⁹ and $-10 \text{ cal deg}^{-1} \text{ mol}^{-1}$ was taken as a reasonable estimate of ΔS° for CTC formation. Accordingly, the binding energy (ΔH°) of the P3HT·O₂ CTC was estimated to be -10.6 kJ/mol (0.11 eV).

ϵ_{eff} , an effective extinction coefficient of the complex, is expressed below and is the sum of the extinction coefficient of the 1:1 CTC and that due to the “contact” component.^{15b}

$$\epsilon_{\text{eff}} = \epsilon_{\text{CTC}} + \frac{\alpha \overline{\epsilon_{\text{DA}}}}{K_c} \quad (13)$$

α is the number of contact sites of the donor around the acceptor, and $\overline{\epsilon_{\text{DA}}}$ is the extinction coefficient of the “contact” CTC. α values of 4–5 have been previously estimated for iodine–benzene complexes in solution.^{15b} From the restricted geometry of solid polymers we anticipate α to be less than this value. For low equilibrium constants, $\epsilon_{\text{CTC}} = \overline{\epsilon_{\text{DA}}}$, so that the relatively large value for ϵ_{eff} is certainly indicative of a contact charge transfer complex in concordance with Mulliken's theory of molecular complexes.^{15c}

EPR. EPR spectra of P3HT were obtained under reduced pressure (4 mmHg) in air and 1 atm of O₂. Analysis of the data indicates that introduction of oxygen gives rise to a small increase in the EPR signal. The data show a reversible interaction between O₂ and P3HT.

At 1 atm of oxygen, the polymer's EPR signal exhibits a Gaussian line shape with a peak-to-peak width of 6.00 G and a g -value of 2.0032. Similar EPR results were obtained in air. At reduced pressure (4 mmHg), the peak-to-peak width was found to decrease to 5.57 G while the g -value increased to 2.0039. The concentrations of spins were determined from integrals of the EPR signals. Under vacuum, the polymer was found to contain $5.4 \times 10^{17} \text{ spins/g}$ ($\sim 4.9 \times 10^{17} \text{ spins/cm}^3$). Introduction of oxygen at a pressure of $\sim 1 \text{ atm}$ resulted in an increase in the spin density to $7.1 \times 10^{18} \text{ spins/g}$ ($\sim 6.4 \times 10^{18} \text{ spins/cm}^3$), which is consistent with the value of $3 \times 10^{18} \text{ spins/cm}^3$ obtained for the CTC concentration at 1 atm of O₂ estimated by using the equilibrium constant K_c .

The observed increase in intensity of the polymer's EPR absorption in the presence of oxygen is indicative of the ionic character of the P3HT·O₂ CTC, i.e., P3HT and O₂ contain unpaired electrons.²⁰ The g -value ($g = 2.0023$) is typical of free electrons, indicating that the electrons are delocalized on the polymer backbones. The oxygen radical anions, O₂^{•-}, give broad absorption lines that are not resolved at atmospheric pressure.²¹ The P3HT·O₂ CTC can thus be represented as shown in Figure 6.

Electronic Properties. A charge transfer complex between the polymer and O₂ might facilitate the generation of charge

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(17) If the concentration of the donor was estimated based on an octamer or tetramer, then [CTC] was calculated to be $\sim 1.7 \times 10^{-3}$ and $0.86 \times 10^{-3} \text{ M}$, respectively.

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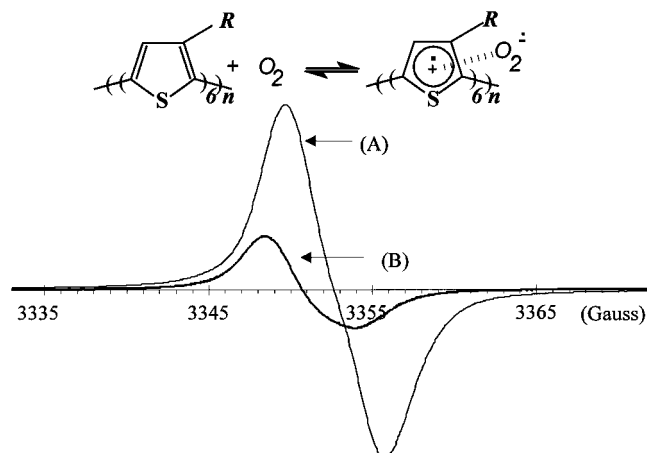


Figure 6. (Top) Representation of the poly(3-alkylthiophene)–oxygen charge transfer complex. (Bottom) EPR spectra of P3AT: (a) in air and (b) in vacuum.

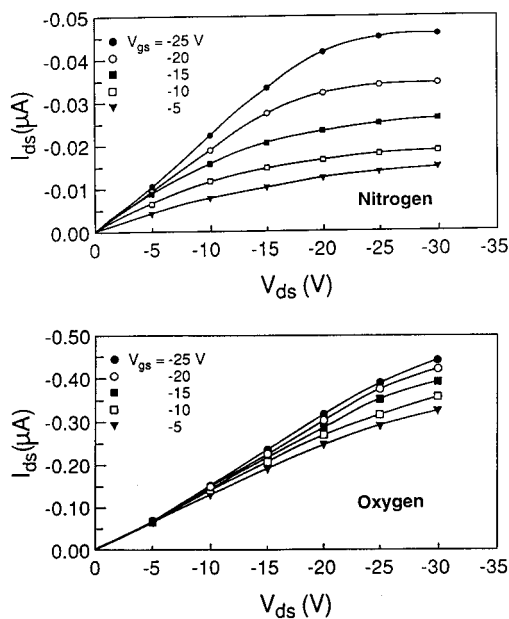


Figure 7. I_{DS} – V_{DS} characteristics of polymer-FETs in the absence and presence (10 atm) of O_2 .

carriers upon application of an electric field across polymer films. In order to evaluate this, thin film field effect transistors (FETs) incorporating π -conjugated polymers were used to characterize electrical parameters of the materials in the presence and absence of oxygen. These microelectronic structures are particularly useful since charge generation and charge migration processes can be separated, and information on charge carrier concentration, charge mobility, and conductivity extracted. Several reports have indicated that polythiophene-based FETs are sensitive to the presence of oxygen.^{4d,e,6} Here we correlate electrical parameters of devices with the P3HT– O_2 charge transfer complexes by studying P3HT-FETs under different pressures of oxygen (0–10 atm).

Figure 7 shows FET characteristics under vacuum and under 10 atm of oxygen. In the absence of oxygen, a typical FET-like response is observed, i.e., clear saturation currents which are proportional to the gate bias. In the presence of oxygen, the current increases by an order of magnitude and the curves take on considerable “ohmic” behavior. These I – V curves are fully reversible upon the removal or addition of oxygen. The carrier mobility decreases with increasing oxygen pressure (Figure 8). This inverse relationship indicates that the carrier concentration is increasing with pressure. Under high oxygen

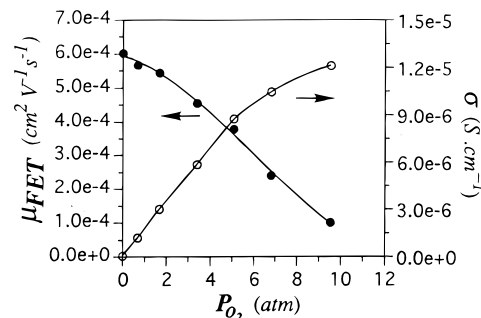


Figure 8. Effect of oxygen pressure on the charge carrier mobility and conductivity of P3HT films.

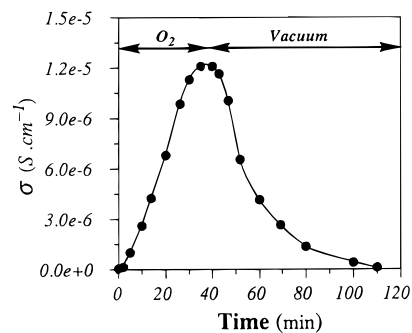


Figure 9. Time response for change in conductivity of P3HT thin films upon application and removal of O_2 . $p(O_2) = 10$ atm.

pressures, the carrier concentration at the polymer/insulator surface is sufficiently large that surface scattering of carriers occurs and mobility decreases. The conductivity of the films ($\sigma = ne\mu$) increases linearly with low oxygen pressure (4×10^{-8} S/cm in *vacuo*), 4×10^{-7} S/cm at $p(O_2) = 0.2$ atm, and 2×10^{-6} S/cm at $p(O_2) = 1$ (atm) and nonlinearly with higher pressures due to scattering effects. The observation that the mobility decreases with increasing carrier concentration is similar to that observed for P3AT thin-film transistors in the presence of increasing concentrations of impurities²² and consistent with most inorganic semiconductors, but it is in contradiction with general observations that carrier mobility in conjugated polymers increases with the degree of doping.²³ However, it should be recognized that the latter studies usually utilize counterions which help delocalize and stabilize the positive charge carriers on the polymer. In the case of O_2 and impurity doping²² the counterions are far from ideal, and it can be argued that this results in a more localized charge distortion and a more effective scattering center.

The change in conductivity upon contact with oxygen is also indicated in Figure 9. This plot indicates the time response of the film upon application of oxygen or vacuum. We associate the long equilibration time with slow diffusion of oxygen into the bulk polymer. It must be borne in mind that thin films of P3HT are semicrystalline, and this will serve to retard diffusion. In the case of oligothiophenes, it was shown that the change in conductivity upon exposure to oxygen took several days to reach equilibrium.²⁴ This is presumably the result of the larger degree of crystallinity associated with oligothiophenes and the extremely slow rate of oxygen diffusion in these films. In addition to providing valuable information on the interactions between conjugated polymers and oxygen, these FETs are attractive as

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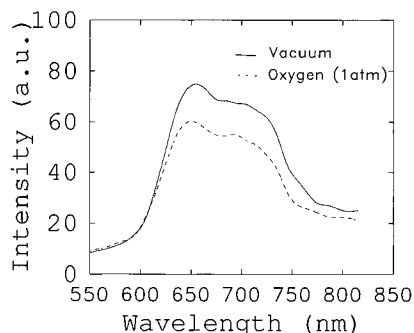


Figure 10. Fluorescence spectra of P3HT film *in vacuo* and under O₂ (1 atm). $\lambda_{\text{ex}} = 480$ nm.

oxygen sensors since the sensing material can be spatially deposited with micron resolution by microlithographic techniques and can be easily integrated into microelectronic circuitry as active components. For such applications it will be necessary to substantially reduce the response time of devices.

Fluorescence Quenching. Solutions and films of P3HT fluoresce when the $\pi-\pi^*$ band is irradiated. For polymers possessing $\sim 80:20$ HT:HH dyad content quantum yields of fluorescence are 0.14 and 0.002 for polymer solutions and polymer films, respectively.^{2b} In the presence of oxygen, quantum yields are 0.07 and 0.00017, respectively, i.e., solution fluorescence is quenched by 50%, and film fluorescence is quenched by 18%. This degree of quenching cannot be explained by Stern–Volmer collisional quenching theory for the following reasons. According to the Stern–Volmer relation, the ratio of the intensity of luminescence in the presence and absence of oxygen quencher is estimated from $I_0/I = 1 + k_q\tau[\text{O}_2]$.²⁵ In solution, we can assume the quenching rate constant, k_q , is diffusion controlled ($\sim 10^{10} \text{ M}^{-1} \text{ s}^{-1}$),¹⁸ $\tau \sim 600$ ps,^{3c} and $[\text{O}_2]_{\text{soln}} \sim 0.01 \text{ M}$.²⁶ A Stern–Volmer analysis accounts for an upper limit of only 6% quenching in solution in contrast to the 50% quenching experimentally observed. In the solid state, the lifetime of the excited singlet state is even shorter (< 100 ps).^{3c} Taking $[\text{O}_2]_{\text{film}}$ as 0.015 M at 1 atm of O₂, collisional quenching predicts a 0.3% quenching efficiency. Experimentally, fluorescence is quenched by 18% by the presence of oxygen in sharp contrast to the predicted value (Figure 10).

Clearly, oxygen quenches luminescence through a different mechanism than that of collisional quenching. A mechanism involving quenching excitation through the P3HT–O₂ charge transfer complex seems plausible. Indeed, several studies have shown that polaronic and bipolaronic charged states serve as centers for nonradiative deactivation of excited singlet states in conjugated polymers.²⁷ Accumulation layers formed in thin polymer films by application of voltage biases to metal–insulator–semiconductor (MIS) structures have been shown to quench photoluminescence of P3ATs.²⁸ For thick films (50–100 nm), photoluminescence is quenched in MIS structures by $\sim 5\%$. However, for Langmuir–Blodgett (LB) films (10–20

nm thick), luminescence quenching is as high as 25%. The difference in quenching efficiency can be explained in terms of the fraction of the accumulation layer with respect to the total film thickness. In the case of LB films, the charge density was estimated to be less than one charge per 10^4 thiophene rings, which indicates that the number of quenching centers required for effective luminescence quenching is relatively low.²⁹

The polymer–O₂ CTC is present in a concentration of $1 \times 10^{-3} \text{ M}$, which translates into a relative CTC to thiophene–monomer ratio of 1 to 6×10^4 (i.e., $2 \times 10^{-5} \text{ mol } \%$ doping). The degree of quenching observed for this charge concentration is consistent with data from MIS structures. We also note that energy migration of polaron excitons to quenching centers should be facile, and will dominate the kinetics and efficiency of quenching since energy migration will be much more rapid than physical diffusion of the charge transfer complex. The diffusional length of excitons is determined by their rate of migration and lifetime. Hayashi et al. have found that the diffusion length of excitons in polythiophene films is ~ 26 nm (70 thiophene rings) based on the modeling of luminescence quenching using a 1-D migration of excitons,^{24d} whereas Bässler et al., studying photoconduction in poly(3-alkylthiophenes), have concluded an exciton diffusion length of 60 nm (162 rings).³⁰ The difference between the two values most likely reflects inherent differences between the two polymers. For a [CTC] $\sim 1 \times 10^{-3} \text{ M}$, the charge transfer complexes are calculated to have a separation distance of ~ 12 nm (32 rings) on average, based on a simple 3-D lattice model. This distance of separation is not dissimilar to the diffusional length of the exciton determined by Hayashi and Bässler. Thus the CTC appears to be of sufficient concentration to effect the quenching of excitation during its inherent lifetime.

Discussion

There is ample precedence of charge transfer complexes of oligo- and polythiophenes with π -acceptors such as tetracyanoquinodimethane.³¹ Charge transfer bands are observed but conductivities are modest (10^{-6} – 10^{-9} S/cm). Exceptions are the high conductivities of α -sexithienyl-Keggin-type heteropolyanions ($\sigma \sim 3 \text{ S/cm}$)³² and thiophene-fused tetracyanoquinodimethane–TTF complexes ($\sigma \sim 5 \text{ S/cm}$).³³ Our results provide experimental evidence for a reversible interaction between poly(3-alkylthiophenes) and oxygen to form a charge transfer complex. While this CTC is inherently weak, and hence can be considered largely a “contact” CTC, the steady state concentration of the CTC is sufficient to affect the luminescence, electroluminescence, and electronic properties of these polymers. In addition, the CTC may be pivotal to the photochemistry of P3ATs. It is known that these polymers are susceptible to extensive photodegradation in the presence of oxygen. The dominant reaction leading to degradation is photobleaching, which involves photosensitization, and reaction, of singlet

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(29) From studies of fluorescence quenching as a function electrochemical doping, Hayashi et al. (ref 27d) have determined that a much higher number of charge carriers are required to produce the same degree of doping. However, their results were obtained in the high doping regime where bipolaron formation is favored.

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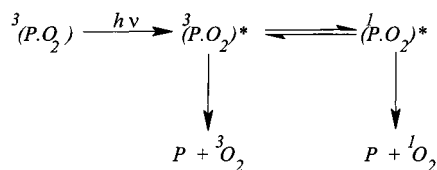


Figure 11. Proposed mechanism for the generation of singlet oxygen via the charge transfer complex.

oxygen.^{9,34} Photosensitization of singlet oxygen by triplet states of polythiophene seems unlikely, given the recent phosphorescence and transient spectroscopic data which indicate a very low quantum yield of triplet formation.³⁵ An alternative explanation for photosensitization of singlet oxygen is based on dissociation of an excited state CTC. Recently, Ogilby et al. have illustrated photogeneration of singlet oxygen in polystyrene by irradiation of oxygen–polystyrene charge transfer complexes.³⁶ One can anticipate π -conjugated polymers as being more susceptible to CTC formation than polystyrene since the former exhibit much lower ionization potentials. Such a mechanism of photosensitization is shown below (Figure 11).

There are several X-ray photoelectron spectroscopic studies concerning the nature of the interaction of oxygen, and other dopants, with polythiophenes.³⁷ Some state the positive charge resides on the ring, others imply it resides on the sulfur, and others still claim it is on both the carbons and sulfur. At present it appears inconclusive. Our results indicate charge withdrawal

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occurs from the delocalized π -system of the conjugated polymer, but more work is required to elucidate the exact nature of the chemical interaction between P3HT and O₂.

Conclusions

In summary, oxygen forms a weak charge transfer complex with conjugated poly(3-alkylthiophenes). The complex exhibits an absorption maximum in the visible region of the spectrum as predicted from empirical relationships. The CTC is largely responsible for the generation charge carriers in semiconducting π -conjugated polymers exposed to air. The conductivity of the polymer increases with oxygen pressure. Because these polymers act as both the amplifying and sensing medium, thin-film transistors using poly(3-alkylthiophenes) might prove to have interesting oxygen-sensor applications. The complex is an efficient quencher of excitation. Quenching can be explained by the antenna effect wherein the polymer backbone is an efficient medium by which excitons can migrate to quenching sites.

The formation of a charge transfer complex with π -conjugated polymers is predicted to be a general effect. The degree of charge transfer and the magnitude of the equilibrium constant of complex formation will certainly be a function of the ionization potential and morphology. Those polymers possessing low ionization potentials and having an amorphous nature, to facilitate diffusion of oxygen into the bulk, will be particularly susceptible to charge transfer complex formation in the presence of oxygen. The degree of charge transfer is expected to increase as the ionization potential of the polymer is lowered. In the extreme case, a full electron transfer can occur between the polymer and oxygen as is known to occur for polypyrroles.

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