

Photochemistry of Electronically Conducting Poly(3-alkylthiophenes) Containing FeCl_4^- Counterions

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Irradiation of electronically conducting poly(3-alkylthiophenes) doped with the FeCl_4^- counterion results in a loss of electronic conductivity ($6 \text{ S/cm} \rightarrow 10^{-5} \text{ S/cm}$). The mechanism proceeds by (i) direct photolysis of FeCl_4^- and (ii) photoreduction of FeCl_4^- to FeCl_4^{2-} followed by (iii) electron transfer to bipolaronic residues. Upon prolonged photolysis the products are neutral, nonconductive polymer and octahedral iron(III) complexes. Photochemical dedoping occurs *in vacuo* but is greatly accelerated by moisture. The reaction is sufficiently facile to occur significantly under ambient light. Replacement of FeCl_4^- with a less photolabile counterion, AuCl_4^- , results in a several orders of magnitude increase in the longevity of the irradiated conducting polymer. Photochemical mechanisms responsible for these observations are described.

Introduction

The unique properties of polythiophenes, and conducting polymers in general, are due to the existence of π -conjugation along the main chain.¹ As a result of π -conjugation, these materials are electrochromic, exhibit third order nonlinear activity and semiconductivity, and can be easily oxidized so as to impart high electronic conductivity. Polythiophene itself is an intractable solid. However, derivitization of the thienyl rings at the 3-position with long alkyl chains, for example, yields polymers which are soluble in common organic solvents.² Soluble polythiophenes have the advantage of ease of characterization and processability, but often the stability of the oxidized conducting form is compromised compared to the parent polymer.

Significant effort has been made toward understanding the instability of conducting poly(3-alkylthiophenes), and several groups have provided valuable insights into this rather complex phenomenon.³ The reversion of the conductive form to the neutral, semiconducting counterpart is, in essence, a reductive electron-transfer process.

This process is commonly termed *dedoping*; and this description, while technically incorrect, is used throughout this paper because of its common usage. The majority of studies to date have been concerned with thermal dedoping processes of P3ATs containing the FeCl_4^- counterion since this polymer-counterion combination is reportedly the most thermally stable. It has recently been shown however that dedoping of this system can occur photolytically.⁴ Indeed, for thin films ($<1 \mu\text{m}$), photolytic dedoping dominates over thermal dedoping under ambient lighting.⁵

In this report, we describe the mechanism of photolytic dedoping of P3ATs doped with the FeCl_4^- counterion. The study employs poly(3-hexylthiophene) (P3HT) as the model π -conjugated polymer.

Experimental Section

Chemicals and Instrumentation. Anhydrous ferric chloride (BDH Chemicals), gold trichloride (Aldrich Chemicals) and ammonia solution (BDH) were used as received. Chloroform (Caledon, spectral grade) and THF (BDH, HPLC grade) were also used as received. Acetonitrile and nitromethane (spectral grade, BDH) were dried over CaH_2 and activated alumina, respectively. UV-vis-NIR spectra were recorded on a Perkin-Elmer Lambda 3A UV-vis spectrophotometer and Cary 17 (Varian Instruments) at 25 °C. Infrared spectra were recorded on a Bomem Michelson FTIR (120 series). The thickness of the polymer films was measured using a stylus profilometer (Tencor Instruments, Alpha-step 200).

Mössbauer spectra were recorded at 77 K on a constant-acceleration Harwell Instruments spectrometer (200 series) with a $^{57}\text{Co/Rh}$ source (New England Nuclear). The 35.5 keV Mössbauer γ -ray was monitored Kr/ CO_2 proportional counter. The spectra were accumulated in a Nuclear Data 66 analyzer as 256-channel spectra and were subsequently computer-fitted to Lorentzians. The acquisition time of individual measurements was 10 days. Absorbers containing ca. 80 mg of polymer sample ($\sim 8 \text{ mg Fe}$) were mounted in Teflon holders in oxygen-free nitrogen. The cross-sectional area of the sample was 2 cm^2 . Samples photolyzed *in vacuo* were transferred in a drybox into the Teflon holder and sealed with silicon grease. Isomer shifts are quoted with respect to iron metal.

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(1) (a) Yamamoto, T.; Sanechika, K.; Yamamoto, A. *J. Polym. Sci., Polym. Lett. Ed.* 1980, 18, 9. (b) Tourillon, G.; Garnier, F. *J. Electroanal. Chem.*, 1982, 135, 173. (c) Skotheim, B., Ed. *Handbook of Conducting Polymers*; Marcel Dekker: New York, 1986; Vols. 1, 2. (d) Bredas, J. L., Silbey, R., Eds., *Conjugated Polymers*, Kluwer Academic: Dordrecht, The Netherlands, 1991.

(2) (a) Elsenbaumer, R. L.; Jen, K. Y.; Oobodi, R. *Synth. Met.* 1986, 15, 169. (b) Sato, M.; Tanaka, S.; Kaeriyama, K. *J. Chem. Soc., Chem. Commun.* 1986, 873. (c) Roncali, J. *Chem. Rev.* 1992, 92, 711.

(3) (a) Billingham, N. C.; Calvert, P. D.; Foot, P. J. S.; Mohammad, F. *Polym. Degrad. Stab.* 1987, 19, 323. (b) Tourillon, G.; Garnier, F. *J. Electrochem. Soc.* 1987, 130, 2042. (c) Jen, K. Y.; Miller, G. G.; Elsenbaumer, R. D. *J. Chem. Soc., Chem. Commun.* 1986, 1346. (d) Druy, M. A.; Rubner, M. F.; Walsh, S. P. *Synth. Met.* 1986, 13, 207. (e) Wang, Y.; Rubner, M. F. *Synth. Met.* 1990, 39, 153; 1991, 41-43, 1103. (f) Wang, Y.; Rubner, M. F. *Macromolecules* 1992, 25, 3284. (g) Gustafsson, G.; Inganäs, O.; Nilsson, J. O.; Liedberg, B. *Synth. Met.* 1988, 26, 297. (h) Pei, Q.; Inganäs, O. *Synth. Met.* 1992, 46, 353. (i) Pei, Q.; Jarvinen, H.; Osterholm, J. E.; Inganäs, O.; Laasko, J. *Macromolecules* 1992, 25, 4297. (j) Osterholm, J. E.; Passiniemi, P.; Isotalo, H.; Stubb, H. *Synth. Met.* 1987, 18, 213. (k) Lojonen, M. T.; Tak, T.; Laasko, J.; Vakiparta, K.; Suuronen, K.; Valkainen, P.; Osterholm, J. E. *Synth. Met.* 1991, 41-43, 479. (l) Isotalo, H.; Ahlskog, M.; Stubb, H.; Laasko, J.; karna, T.; Jussila, M.; Osterholm, J. E. *Synth. Met.* 1993, 55-57, 3581. (m) Taka, T. *Synth. Met.* 1993, 55-57, 4985. (n) de Leeuw, D. M. *Synth. Met.* 1993, 55-57, 3597. (o) Daoust, D.; Leclerc, M. *Macromolecules* 1991, 24, 455.

(4) (a) Abdou, M. S. A.; Holdcroft, S. Presented at the 76th Canadian Society for Chemistry Congress, Sherbrooke, Quebec, May 30-June 3, 1993, Abstract No. 249. (b) Sandberg, M.; Tanaka, S.; Kaeriyama, K. *Synth. Met.* 1993, 55-57, 3587.

(5) Abdou, M. S. A.; Holdcroft, S. *Polymer Prepr. (Am. Chem. Soc., Div. Polym. Chem.)*, in press.

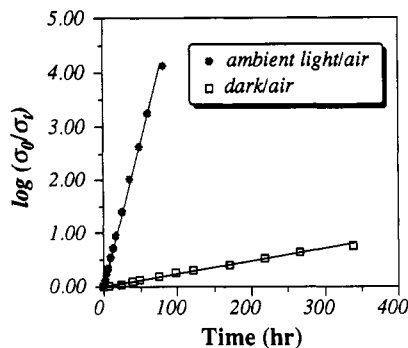
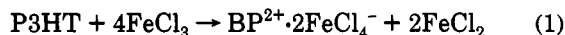


Figure 1. Decrease in σ of P3HT-FeCl₄⁻ films during exposure to ambient light. Ambient laboratory conditions: relative humidity 25, 298 K. Thermal dedoping at 298 K in the dark is shown for comparison. Film thickness 0.25 μm , $\sigma_0 \sim 6 \text{ S cm}^{-1}$.

Polymer Synthesis. Polymerization was achieved by chemical oxidative coupling according to the procedure described by Sugimoto et al.⁶ The solid product was filtered and washed successively with NH₃ solutions (28%), water and finally acidified methanol. The crude polymer was dissolved in hot dichloromethane, and insoluble products were removed by filtration. The polymer was precipitated by adding methanol. The precipitate was filtered and low molecular weight products were removed by Soxhlet extraction. The solid polymer was finally dried under reduced pressure at 50 °C. The number average molecular weight, M_n , was 8500, and the molecular weight distribution was ~ 3 . Details of molecular weight analysis have been previously reported.⁷ The head-to-tail: head-to-head dyad ratio was 80:20, as determined by ¹H NMR, giving a λ_{max} in CHCl₃ of 435 nm.⁸ Polymers prepared by this method were found to contain residual iron salts even after extensive purification. The concentration of iron in crude polymer was 3.2 wt % as determined by atomic absorption. Rigorous reprecipitation reduced the iron content to 0.05 wt %. The oxidation state of this iron species was +3 as determined by Mössbauer spectroscopy. Iron-free polymer was prepared for Mössbauer measurements by electrochemical polymerization of 3-hexylthiophene.

Chemical Doping. Thin films of P3HT (0.25 μm), spin-cast (2000 rpm, 30 s) onto quartz slides from chloroform solutions, were oxidatively doped using solutions of FeCl₃ (0.1 M) in dry nitromethane. The doped samples were washed with fresh nitromethane and dried under vacuum in the dark. The level of doping was determined by elemental analysis and mass uptake measurements to be $\sim 24 \text{ mol } \%$ based on repeating thienyl units. Tetrahedral FeCl₄⁻ is the dominant iron species incorporated in the polymer following oxidation. This assertion is made on the basis of elemental analysis (Fe:Cl = 1:4); UV-vis-NIR spectroscopy (λ_{max} : 240, 316, and 368 nm);⁹ and Mössbauer spectroscopy (quadrupole doublet: isomer shift, δ , of 0.253 mm s⁻¹ and quadrupole splitting, Δ , of 0.284 mm s⁻¹).¹⁰

The mechanism of oxidation of P3HT is shown in the following scheme:¹¹



where BP²⁺ represents the bipolaronic charge carriers and FeCl₄⁻

Table 1. Effect of Irradiation on the Decrease in Conductivity of Oxidized Poly(3-hexylthiophene)-FeCl₄ Films^a

conditions ^b	$t_{1/2}$ (min) ^c
ambient light ^d /air	114
366 nm/air	0.9
435 nm/air	40
580 nm/air	5790
dark/air	5830

^a Film thickness 0.25 μm , 298 K. ^b Relative humidity of ambient air 25. ^c Half-life time of decrease in conductivity. Data for 366, 435, and 580 nm are normalized for absorbed irradiation dose. ^d Fluorescent lighting.

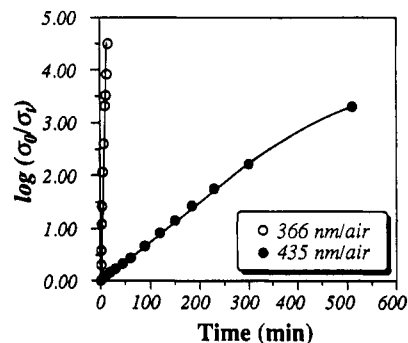


Figure 2. Effect of irradiation wavelength on the photochemical reduction of P3HT-FeCl₄⁻ films. Ambient laboratory conditions: relative humidity 25, 298 K. Film thickness 0.25 μm , $\sigma_0 \sim 6 \text{ S cm}^{-1}$. The plots are normalized for quanta of light absorbed.

is the counterion. FeCl₂ formed during the course of the oxidation process precipitates from solution.¹² Mössbauer spectroscopy of doped polymers indicated the absence of iron(II).¹³ Electronic conductivities were measured on thin films by the four-point-probe technique.

Photolyses. The illumination source was a 150-W mercury lamp (Illumination Industries Ltd.) focused to a 4 cm² beam. Irradiation was carried out using a 300-nm cutoff filter unless stated otherwise. For several experiments, the wavelength of irradiation was selected using an appropriate 10-nm bandwidth interference filter. The temperature of the sample was kept constant at 25 °C using a cooling block and a circulating water bath. The intensity of incident light at 366 was 1.4 mW/cm².

Results

Photolytically Induced Decrease in Conductivity. Oxidized, conducting films of P3HT ($\sigma \sim 6 \text{ S/cm}$) were exposed to ambient laboratory lighting. Figure 1 shows pseudo-first-order kinetic plots for the decrease in conductivity of oxidized polymer films with time. By comparison, the rate of decrease in conductivity in the absence of light is ~ 50 times slower. The half-life time values, $t_{1/2}$, are given in Table 1. This preliminary result illustrates the dramatic effect of light on the stability of P3HT-FeCl₄⁻. The photochemical stability of the polymer-counterion pair was studied using 366-, 435-, and 580-nm monochromatic light. Figure 2 shows the change in conductivity with irradiation time in air using 366- and 435-nm monochromatic light. $t_{1/2}$ values for the decrease in conductivity are 0.9 and 40 min, respectively, for incident intensities normalized to the irradiation dose. Degradation using 366 nm light is 48 times greater than with 435 nm

(12) (a) Morin, A.; Beniere, M.; Beniere, F. *J. Phys. Chem. Solids* 1989, 50, 611. (b) *Philos. Mag. A* 1991, 64, 1073.

(13) The characteristic Mössbauer resonance signal for iron(II) occurs at $\delta \sim 0.9 \pm 0.1 \text{ mm s}^{-1}$.

(6) Sugimoto, R.; Takeda, S.; Gu, H. B.; Yoshino, K. *Chem. Express* 1986, 1, 635.

(7) (a) Holdcroft, S. *J. Polym. Sci., Polym. Phys. Ed.* 1991, 29, 1585.

(b) Holdcroft, S. *Macromolecules* 1991, 24, 4834.

(8) Mao, H.; Xu, B.; Holdcroft, S. *Macromolecules* 1993, 26, 1163.

(9) (a) Day, P.; Jorgensen, C. K. *J. Chem. Soc.* 1964, 6226. (b) Friedman, H. L. *J. Am. Chem. Soc.* 1952, 74, 5. (c) Swanson, T. B.; Laurie, V. W. *J. Phys. Chem.* 1965, 69, 244.

(10) (a) Greenwood, N. N.; Gibb, T. C. *Mössbauer Spectroscopy*, Chapman and Hall: London, 1971. (b) Edwards, P. R.; Johnson, C. E. *J. Chem. Phys.* 1968, 49, 211. (c) Pron, A.; Fatseas, G. A.; Krichene, S.; Lefrant, S.; Maurice, F.; Froyer, G. *Phys. Rev. B* 1985, 32, 1839.

(11) (a) Fichou, D.; Horowitz, G.; Garnier, F. *Synth. Met.* 1990, 39, 125. (b) Fichou, D.; Horowitz, G.; Xu, B.; Garnier, F. *Synth. Met.* 1990, 39, 243. (c) Fichou, D.; Xu, B.; Horowitz, G.; Garnier, F. *Synth. Met.* 1991, 41-43, 463.

Table 2. Effect of Ambient Conditions on Photochemical Dedoping of Poly(3-hexylthiophene)-FeCl₄⁻ Films^a

conditions	$t_{1/2}$ (min) ^b
laboratory air ^c	0.9
humidified O ₂ ^d	1.4
dry O ₂	3.3
vacuum	5.1

^a Incident wavelength 366 nm ($I_0 = 1.4 \text{ mW/cm}^2$). Film thickness 0.25 μm , 298 K. ^b Half-life time of decrease in conductivity. ^c Relative humidity 25. ^d Relative humidity 15.

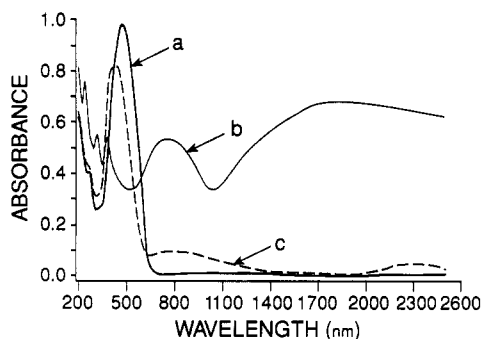


Figure 3. UV-vis-NIR spectra of oxidized P3HT films under ambient atmosphere: (a) pristine, neutral polymer; (b) oxidized polymer; (c) following irradiation with 366-nm light, 298 K, film thickness 0.25 μm .

light.¹⁴ The optical density of FeCl₄⁻ at 366 nm is 47 times larger than at 435 nm, which might account for the difference if direct excitation of FeCl₄⁻ is responsible for photodegradation. Irradiation with 580-nm light did not lead to photodegradation. At this wavelength, light is absorbed only by polymer charge carriers; the extinction coefficient of FeCl₄⁻ is zero. This is direct evidence that photodegradation is primarily due to excitation of the counterion.

Irradiation of doped films with 366-nm light was also conducted under various atmospheres; namely, ambient air (relative humidity, RH, 25%), dry O₂, and *in vacuo*. $t_{1/2}$ values calculated from pseudo-first-order kinetic plots are given in Table 2. Moisture clearly accelerates photochemical degradation.

Spectroscopic Analysis. (i) *UV-Vis-NIR*. The photochemistry of BP²⁺·2FeCl₄⁻ was studied in detail in order to understand the photolytic dedoping processes. Doped polymers show the characteristic bipolaronic electronic transitions at 750 and $\sim 1750 \text{ nm}$ ^{15,16} (Figure 3), in addition to absorption bands at 240, 316, and 368 nm due to FeCl₄⁻.⁹ The change in UV-vis-NIR absorption spectra of oxidized polymer films exposed to 366-nm light in ambient air is also shown in Figure 3. The absorption bands due to FeCl₄⁻ decrease, indicating loss of FeCl₄⁻. A broad band emerges at $\sim 485 \text{ nm}$ due to the π - π^* transition of the neutral polymer. Bipolaron absorption bands at 750 and $\sim 1750 \text{ nm}$ concurrently decrease. The spectra evolve in a similar manner when either 435-nm monochromatic irradiation or ambient light is employed.

Kinetic analysis shows that the bipolaron concentration decreases in a pseudo-first-order manner during photolysis.

(14) Comparable light intensities at 366 and 435 nm were adjusted using neutral density filters.

(15) (a) Hotta, S.; Rughooputh, S. D. D.; Heeger, A. J.; Wudl, F. *Macromolecules*, 1987, 20, 212. (b) Nowak, M. J.; Rughooputh, S. D. D.; Hotta, S.; Heeger, A. J. *Macromolecules* 1987, 20, 965. (c) Nowak, M. J.; Spiegel, D.; Hotta, S.; Heeger, A. J.; Pincus, P. A. *Macromolecules* 1989, 22, 2917.

(16) Patil, A. O.; Heeger, A. J.; Wudl, F. *Chem. Rev.* 1988, 88, 183.

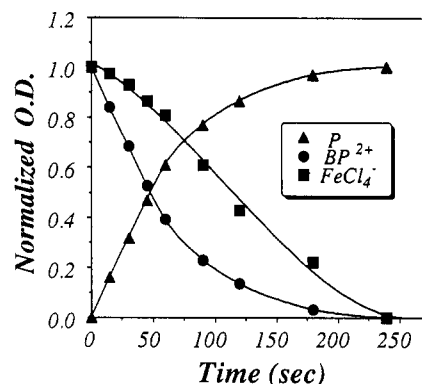


Figure 4. Kinetic plots of the decrease of optical density of P3HT-FeCl₄⁻ films with irradiation time. Irradiation at 366 nm under ambient atmosphere.

A plot of optical density at 750 and 485 nm versus irradiation time is shown in Figure 4. In contrast, the rate of loss of FeCl₄⁻ is not first order. Loss of FeCl₄⁻ is much slower during the initial stages of photolysis. Prolonged photolysis leads to the complete disappearance of FeCl₄⁻. Mössbauer spectroscopic measurements on photolysed samples in air yields a quadrupole doublet with $\delta = 0.42 \text{ mm s}^{-1}$ and $\Delta = 0.60 \text{ mm s}^{-1}$, consistent with an octahedral iron(III) complex.^{10,17} Elemental analysis of photolyzed samples yields a molar Fe:Cl ratio of 1:1.6, which indicates loss of Cl during photolysis.

(ii) *FTIR*. FTIR was used to probe chemical changes of the polymer chain as a result of irradiation. Chemical doping results in broad absorptions in the IR region 4000–600 cm^{-1} . Figure 5 shows FTIR spectra of doped films prior to photolysis and following photolysis. Steady state FTIR spectra were obtained after 5 min of photolysis, beyond which prolonged photolysis resulted in no additional spectral change. It should also be noted that no additional decrease in conductivity ($\sigma \sim 10^{-5} \text{ S/cm}$) was observed following this extended period of photolysis. The persistent broad FTIR spectrum is attributed to residual charge carriers. Photolyzed films were therefore subjected to a reducing atmosphere of ammonia gas following irradiation in order to compensate for residual polaronic and bipolaronic species and enable examination the chemical nature of the polymer chain following photolysis.¹⁸ The reduced, photolysed polymer acquired a new IR band at 1667 cm^{-1} (C=O) and a broad band at 3500 cm^{-1} (OH) relative to the pristine polymer, in addition to those associated with NH₄⁺ (1414, 3050, 3145 cm^{-1}).¹⁹ Noteworthy is the reduction in intensity of the C-H stretching at $\sim 2900 \text{ cm}^{-1}$. This will be discussed later as being evidence for reactions involving the alkyl side chain.

Photochemistry in Vacuo: Evidence of an FeCl₄²⁻ Intermediate. Results obtained from the decrease in conductivity as a function of the wavelength of incident

(17) Dezsai, I.; Vertes, A.; Komor, M. *Inorg. Nucl. Chem. Lett.* 1968, 4, 649.

(18) To clarify that reduction with NH₃ proceeded as a redox reaction only, FTIR spectra were recorded prior to doping, immediately following doping, and following subsequent chemical reduction with ammonia gas. The chemically reduced sample exhibited an identical FTIR spectrum to that of the pristine, neutral polymer with the exception of absorption bands at 3330–3100 and 1485 cm^{-1} due to NH₄⁺. No C-N stretching vibrations (i.e., at $\sim 1075 \text{ cm}^{-1}$) were observed (Foot, P.; Ritchie, T.; Mohammad, F. *J. Chem. Soc., Chem. Commun.* 1988, 1536.)

(19) Bellamy, L. *Advances in Infrared Group Frequencies*; Bellamy, L., Ed.; Methuen & Co. Ltd.: London, U.K., 1968.

(20) Balzani, V.; Carassiti, V. *Photochemistry of Coordination Compounds*; Academic: London, 1970, p.145.

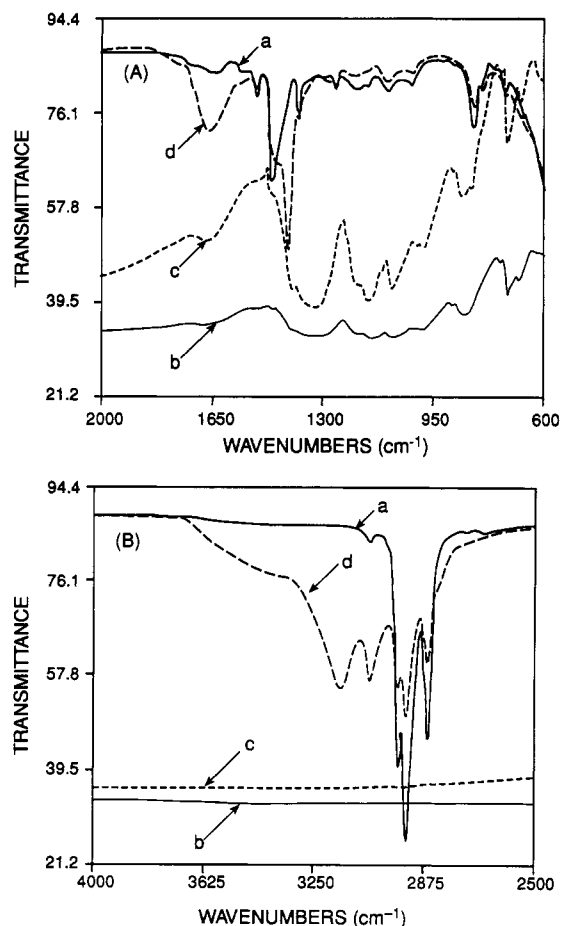
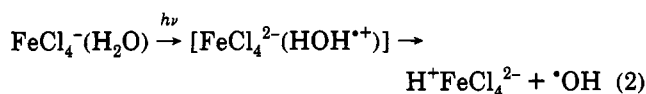


Figure 5. FTIR (A, B) of P3HT films on KBr disks. (a) pristine, neutral polymer; (b) oxidized polymer; (c) following irradiation; (d) same as in (c) but after complete chemical reduction with ammonia vapor. Irradiation wavelength 366 nm; ambient atmosphere.

light indicates photodegradation results from direct photolysis of FeCl_4^- . Indeed, in the presence of moisture, this anion is known to undergo photoreduction:^{20,21}



It is known that Fe(II) salts are oxidized to Fe(III) in the presence of oxygen.²² Thus to determine whether Fe(II) is indeed an intermediate, photolyses were carried out *in vacuo*. Figure 6 shows UV-vis-NIR spectra of photochemically dedoped polymer films using 366-nm light under vacuum. A new absorption band is observed at ~ 2240 nm which is consistent with tetrahedral FeCl_4^{2-} .²³ Mössbauer analysis of the photolyzed sample supports the presence of Fe(II) (quadrupole doublet: $\delta = 0.985$ mm s^{-1} and $\Delta = 1.623$ mm s^{-1} , Figure 7).^{10,24}

(21) (a) Brealey, G. J.; Uri, N. *Nature* **1950**, *166*, 959. (b) Brealey, G. J.; Uri, N. *J. Chem. Phys.* **1952**, *20*, 257. (c) Uri, N. *Chem. Rev.* **1952**, *52*, 357.

(22) Latimer, W. M. *The Oxidation State of the Elements and Their Potentials in Aqueous Solutions*, 2nd ed.; Prentice-Hall: New York, 1952.

(23) (a) Furlani, C.; Cervone, E.; Valenti, V. *J. Inorg. Nucl. Chem.* **1963**, *25*, 159. (b) Burbridge, C. D.; Goodgame, D. M. L., *J. Chem. Soc. A* **1968**, 1410.

(24) Due to the small size of the polymer sample, long acquisition times (10 days) were necessary to accumulate sufficient data for statistical analysis. As a result iron(II) was partly oxidized to iron(III) (0.24 mm s^{-1}) by atmospheric oxygen. After 20 days only iron(III) was observed confirming the oxidation of iron(II) to iron(III).

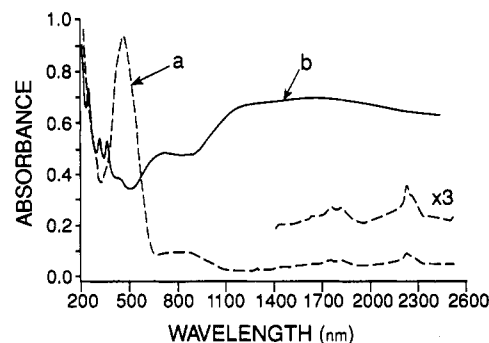


Figure 6. UV-vis-NIR spectra (a) of oxidized P3HT films following irradiation with 366 nm light in *vacuo* and (b) following exposure of photochemically reduced P3HT- FeCl_4^- films to dry oxygen.

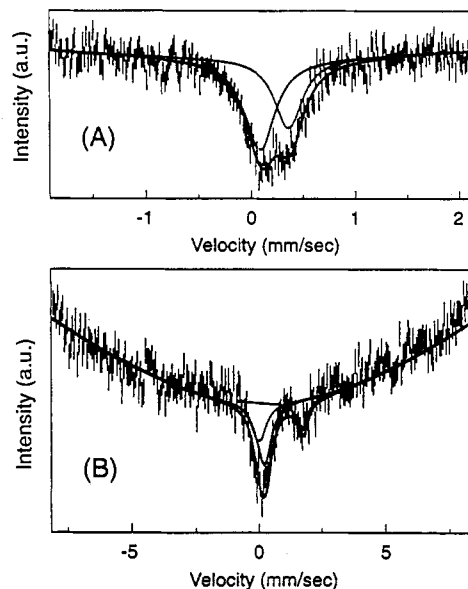


Figure 7. Mössbauer spectra of P3HT- FeCl_4^- films (77 K). (A) oxidized polymer; (B) following irradiation at 366 nm in *vacuo*.

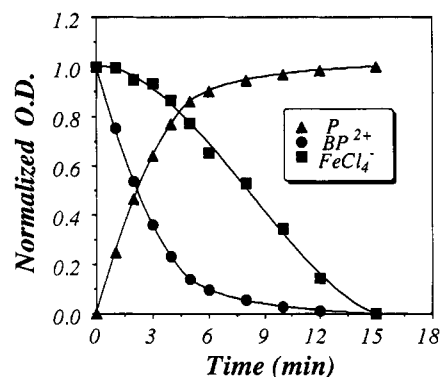
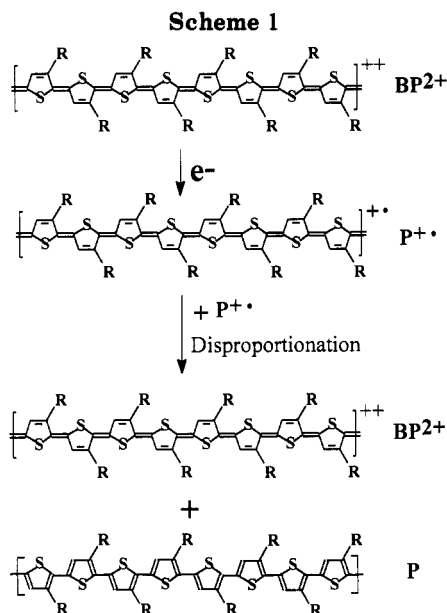


Figure 8. Kinetic plots of the decrease of optical density of P3HT- FeCl_4^- films with irradiation time. Irradiation at 366 nm in *vacuo*.

Similarly to photolysis under ambient atmosphere, the bipolaron concentration decreases in a pseudo-first-order manner during photolysis, whereas the rate of loss of FeCl_4^- is not first order (Figure 8). Initially the concentration of FeCl_4^- remains constant even though polymer is being reduced from its oxidized to neutral form. After prolonged photolysis FeCl_4^- also disappears. The nature of these kinetics and the information they provide on the mechanism of photolysis are discussed later.



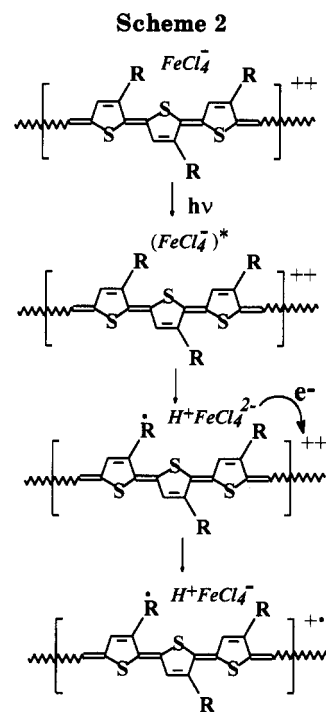
When photolytically dedoped films were exposed to dry oxygen, they reverted to their doped conductive form, and the characteristic absorption bands of FeCl_4^- and BP^{2+} were regenerated Figure 6b. The efficiency of recovery of the doped form was $\sim 90\%$ as calculated from the bipolaron absorption band. The electronic conductivity of the regenerated conducting polymer was 1 S/cm, compared to 6 S/cm for the pristine conducting polymer and 10^{-5} S/cm for the photodoped polymer.

Discussion

Relationship between Bipolarons, Polarons, and Neutral Polymer. In this study we use the term bipolarons and polarons to describe solid-state dications and radical cations, respectively. The precise molecular nature of these species cannot be accurately represented due to uncertainty in the degree of localization. However, it is useful to realize approximate molecular forms of these species in order to understand their photochemical redox reactions.

Contrary to most depictions of bipolarons, the double charge associated with this species must be distributed, on average, over eight thiophyl rings. This assertion is based on the facts that (i) elemental analysis shows the doped polymer as possessing one counter ion for every four rings, (ii) the bipolaron is a doubly charged species, and (iii) UV-vis spectroscopy indicates the absence of neutral conjugated segments at this level of doping. The bipolaron can be thought as comprising two partially delocalized regions of positive charge density which are maximized four thiophyl units apart and which possess minimum charge density in between. The quinoidal character is maximized at the position of highest positive charge density. We assume this position is juxtaposed to the counterion. In this region, interannular bonds possess more double-bond character. In the region of minimum charge density, interannular bonds possess more single-bond character. However, for simplicity, the bipolaronic residue depicted in Scheme 1 is shown as being comprised of quinoidal units rather than the partial-delocalized system.

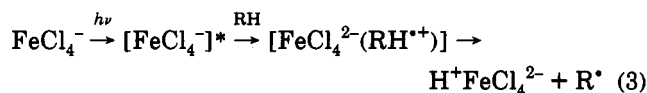
Bipolarons, polarons, and neutral polymer are related by successive one-electron redox reactions, e.g., electron transfer to the bipolaron results in the corresponding



polaron. The charge associated with a polaron may be represented, for simplicity, as being distributed over several rings, with the highest quinoidal character and density of charge being situated close to the location of the counterion. Except for very low concentrations of polarons, polarons are unstable with respect to bipolarons and the following disproportionation process occurs $\text{P}^{+\bullet} + \text{P}^{+\bullet} \rightarrow \text{BP}^{2+} + \text{P}$,²⁵ where P represents neutral polymer. Neutral segments of the polymer will self-interact in order to maximize π -stabilization. The mechanism of reduction of bipolarons to polarons is shown in Scheme 1.

Mechanism of Photodoping. UV-vis-NIR spectroscopy has been used to determine the mechanism of photodegradation of electronically conducting polymers. Photolysis in air and *in vacuo* show similar manifestations associated with reduction of the oxidized polymer, disappearance of FeCl_4^- , and loss of conductivity. However, subtle deviations in these observations provide important information on the photochemical mechanism. Since photolysis *in vacuo* is not complicated by concurrent reactions involving moisture or oxygen, this aspect is treated first.

Photolyses *in Vacuo*. FeCl_4^- is known to undergo photoreduction.^{20,21} In presence of hydrocarbons (RH) photoexcitation is followed by electron transfer and proton transfer:



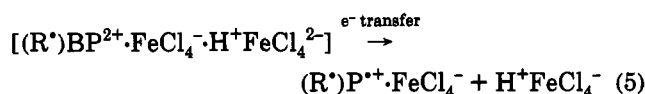
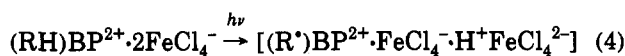
FeCl_4^{2-} is believed to be both an intermediate and a

(25) (a) Harbecke, G.; Meier, E.; Kobel, W.; Egli, M.; Kiess, H.; Tosatti, E. *Solid State Comm.* 1985, 55, 419. (b) Kaufman, J. H.; Colaneri, N.; Scott, J. C.; Street, G. B., *Phys. Rev. Lett.* 1984, 53, 1005. (c) Kaufman, J. H.; Colaneri, N.; Scott, J. C.; Kanazawa, K. K.; Street, G. B., *Mol. Cryst. Liq. Cryst.* 1985, 118, 171. (d) Bredas, J. L.; Themans, B.; Andre, J. M., *Synth. Met.* 1984, 9, 265. (e) Bredas, J. L.; Street, G. B. *Acc. Chem. Res.* 1985, 18, 309. (f) Nechtchein, M.; Devreux, F.; Genoud, F.; Vieil, E.; Pernaut, J. M.; Genies, E. *Synth. Met.* 1986, 15, 59. (g) Bertho, D.; Jouanin, C. *Synth. Met.* 1988, 24, 179. (h) Deussen, M.; Bassler, H. *Synth. Met.* 1993, 54, 49. (i) Tolbert, L. M. *Acc. Chem. Res.* 1992, 25, 561.

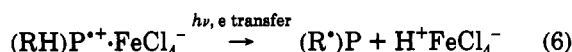
reducing agent in the dedoping reaction. In the present system, there is some doubt as to whether photoreduction of the excited counterion proceeds by electron transfer from the polymer backbone or from the alkyl side chain. However, the data clearly show the doped polymer being photolytically reduced not oxidized beyond its original level.²⁶ Thus, the net reaction must involve oxidation of the side chain followed by rapid proton transfer as illustrated in Scheme 2.

The intermediate, FeCl_4^{2-} , is a strong reducing agent. The formal redox potential of the $\text{FeCl}_4^-/\text{FeCl}_4^{2-}$ couple was determined to be 0.275 V vs SCE whereas the oxidation potential (anodic peak potential) of P3HT was determined to be 0.97 V. Thus FeCl_4^{2-} can thermodynamically reduce BP^{2+} and P^{*+} . Indeed, prepared solutions of $(\text{Et}_4\text{N})_2\text{FeCl}_4$ in acetonitrile completely reduce doped polymer films by simple electron transfer.

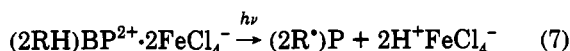
Given that two FeCl_4^- molecules are associated with each bipolaron, the following reaction scheme is proposed:



where (RH) and (R*) represent an alkyl side chain and alkyl radical linked to the polymer backbone. During the initial stages of photolysis, polarons undergo disproportionation to form neutral polymer and bipolarons (see Scheme 1). During the latter stages of photolysis, the polaron can undergo further reduction via



The net overall reaction for the reduction of the oxidized polymer is thus



Kinetic analysis of the photochemical dedoping process (Figure 8) is consistent with photogeneration of FeCl_4^{2-} and subsequent electron transfer from this species to oxidized polymer. Concentration-time profiles for depletion of FeCl_4^- and bipolarons are significantly different. The concentration of FeCl_4^- changes little during initial photolysis while the concentration of bipolarons decreases in a first-order fashion. This observation indicates that FeCl_4^- is regenerated while oxidized polymer is initially reduced, i.e., oxidized polymer is initially photocatalytically reduced by FeCl_4^- .

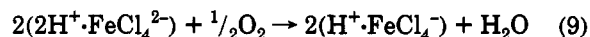
Photolysis of FeCl_4^- does not stop upon photoreduction of the oxidized polymer; prolonged photolysis converts $\text{H}^+\text{FeCl}_4^-$ to $2\text{H}^+ \cdot \text{FeCl}_4^{2-}$, i.e., Fe(III) to Fe(II), by the following reaction:



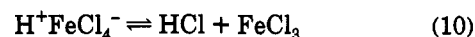
where (RH)P represents a neutral polymer segment possessing pendent alkyl functionality. According to this mechanism, residual iron should be in a +2 oxidation state following photolysis. This was confirmed using NIR spectroscopy by observation of a 2240-nm band (Figure

6) and by Mössbauer spectroscopy (quadrupole doublet: $\delta = 0.985 \text{ mm s}^{-1}$ and $\Delta = 1.623 \text{ mm s}^{-1}$ (Figure 7).

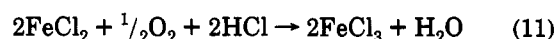
Strong evidence supporting this mechanism is provided by regeneration of the oxidized, conducting form of the polymer upon exposure of photolyzed films to dry oxygen. Oxygen is known to oxidize iron(II) in acid medium.²² The oxidation of $2\text{H}^+ \cdot \text{FeCl}_4^{2-}$ by oxygen proceeds by the reaction



While $\text{H}^+\text{FeCl}_4^-$ is unable to oxidize P3HT, it readily dissociates into HCl and FeCl_3 ($K_{\text{diss}} \sim 95$):²⁷

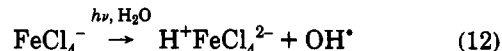


FeCl_3 is a known oxidant for poly(3-hexylthiophene) (see eq 1). Furthermore, FeCl_2 generated from this reaction (eq 1) is oxidized to FeCl_3 in the presence of oxygen and acid:



Conducting polymer containing the FeCl_4^- counterion is thus regenerated almost quantitatively via eqs 9–11 and 1.

Photolyses in Ambient Air. In the absence of moisture we assert the initial photoreduction of FeCl_4^- to FeCl_4^{2-} involves electron transfer from the alkyl functionality attached to the main chain. However, sacrificial electron donors can readily compete with this process. It has been shown, for example, that excitation of FeCl_4^- in the presence of moisture leads to oxidation of water:²¹



Equation 12 is the analogous reaction to eq 3 for which the hydrocarbon, RH, is replaced by H_2O . A series of chemical events follows eq 12 which are analogous to eqs 4–9, except the sacrificial donor is trace water, not the alkyl side chain. A generalized reaction scheme is shown below (Scheme 3).

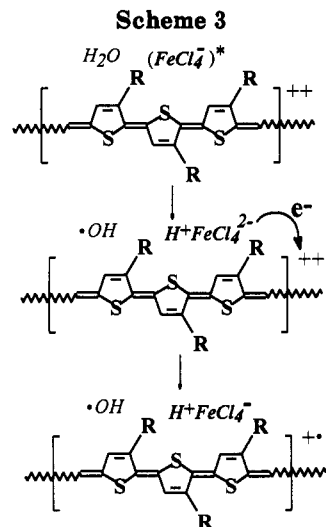
When moisture is the predominant sacrificial electron donor, OH^* radicals are formed. We have previously shown that OH^* radicals abstract H atoms from the alkyl side chain and lead to the formation of polymer-bound aliphatic alcohols as well as cross-linked polymer.²⁸ FTIR confirmed the formation of $-\text{OH}$ groups (Figure 5). In addition, the concentration of aliphatic C–H groups is reduced which is consistent with H abstraction.

During photolysis, FeCl_4^- is converted to an octahedral Fe(III) complex. The reactions by which this occurs cannot be readily described because of the complexity of coordination reactions involving iron species, radicals, and water. We can, however, speculate the mechanism initially

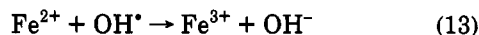
(26) Clearly, electron transfer from the polymer π -system [$\text{P} + (\text{FeCl}_4^-)^* \rightarrow \text{P}^{*+} \cdot \text{FeCl}_4^{2-}$] will be energetically favored over electron transfer from the alkyl side chain, particularly since neutral, electron-rich polymer is produced during the photolysis. However, equally facile will be back-electron transfer resulting in neutral polymer and FeCl_4^- . This does not lead to a net reaction and thus cannot be responsible for the observed photochemistry.

(27) McCusker, P. A.; Kennard, S. M. S. *J. Am. Chem. Soc.* 1959, 81, 2976.

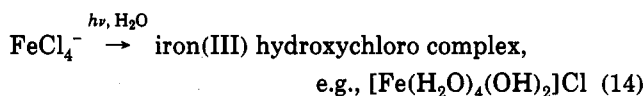
(28) Abdou, M. S. A.; Arroyo, M. I.; Diaz-Quijada, G.; Holdcroft, S. *Chem. Mater.* 1991, 3, 1003. (b) Abdou, M. S. A.; Xie, Z. W.; Leung, A.; Holdcroft, S. *Synth. Met.* 1992, 52, 152. (c) Abdou, M. S. A.; Holdcroft, S. *Macromolecules* 1993, 26, 2954.



involves reaction of hydroxyl radicals with Fe(II) species according to eq 13:²⁹



OH^{-} produced in this process has a strong affinity for coordination with Fe(III). The affinity of Fe^{3+} for OH^{-} is 10^{13} times greater than for Cl^{-} ; thus OH^{-} can displace Cl^{-} in the coordination sphere.^{20c} Elemental analysis of photolyzed films yielded a Fe:Cl ratio of 1:1.6, while Mössbauer spectroscopy revealed the presence of octahedral iron(III). Given this, residual iron is most likely takes the form as an iron(III) hydroxychloro complex in which the cationic charge is compensated by a combination of hydroxy and chloro ions, and in which an octahedral configuration is stabilized by coordination with water.³⁰ A general reaction is



Enhanced Photochemical Stability Using the AuCl_4^{-} Counterion. Armed with the knowledge that

(29) Reaction of OH^{\bullet} with FeCl_4^{2-} is possible, but since the latter is believed responsible for reduction of the polymer it is not expected to be a major pathway until the later stages of photolysis.

(30) Nicholls, D. *Complexes and First-Row Transition Elements*; American Elsevier: Great Britain, 1975; p 177.

photodegradation of P3HT-FeCl_4^{-} is correlated to photolability of the anion, we investigated the photochemistry of oxidized P3HT containing various counterions. The majority of polymer-counterion systems were insufficiently thermally stable that photochemical degradation could not be distinguished from thermal degradation. The exception to this was AuCl_4^{-} -containing conducting polymers which were produced by oxidizing thin films of P3HT with 0.01 M AuCl_3 in acetonitrile. A description of the oxidative-doping process has been previously published.³¹ AuCl_4^{-} is photochemically stable relative to FeCl_4^{-} ,³² and consequently, thin films doped with AuCl_4^{-} are photochemically more stable by several orders of magnitude. $t_{1/2}$ values for the rate of decrease in σ for P3HT-AuCl_4^{-} films are 250 and 30 120 min for irradiation with 366 nm ($I_0 = 1.4 \text{ mW/cm}^2$) and ambient light respectively compared to 0.9 and 114 min for FeCl_4^{-} -containing polymers.

Conclusions

Photodegradation of electronically conducting polymers containing the FeCl_4^{-} counterion is a direct consequence of the photolability of the anion. Photochemical dedoping is an efficient route by which these materials lose conductivity. This is especially true for thin films, for which light penetrates the bulk of the material. The efficacy of this process under ambient lighting can result in considerable errors in conductivity measurements unless precautions are taken to exclude UV light. For thick films, photodoping may be less of a problem since the optical density of the film is such that only the outer surface is penetrated by light. Under ambient conditions moisture is a sacrificial electron donor and accelerates photochemical dedoping. The process cannot be prevented by removing residual water since the polymer itself acts an electron donor. Choosing a photostable counter ion is an obvious solution to photodegradation, but limitations are imposed on the choice of the anion since many polymer-ion systems are thermally labile. In this work we have illustrated enhanced photostability using the AuCl_4^{-} counterion.

Acknowledgment. Financial support of this work by the Natural Sciences and Engineering Research Council of Canada is gratefully acknowledged. The authors thank Drs. R. D. Sharma and C. H. W. Jones for performing Mössbauer spectroscopic analysis.

(31) Abdou, M. S. A.; Holdcroft, S. *Synth. Met.* 1993, 60, 93.

(32) Studzinskii, O. P.; Kartushankii, A. L.; Plachenov, B. T.; *Zh. Obshch. Khim.* (English Transl.) 1985, 55, 673.