

inside the box remained constant to within ± 1 °C.

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Photochemical Formation of Oligothiophene Cation Radicals in Acidic Solution and Nafion

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Three α -coupled terthiophenes, substituted on the terminal positions with methyl, thiomethyl, or bromo substituents, were photooxidized in a solvent mixture of methylene chloride and trifluoroacetic acid to form cation radicals. Visible, near-IR, and ESR spectra are reported. It is shown that the photooxidation requires oxygen and is acid catalyzed. In acetonitrile/trifluoroacetic acid, cation radical π -dimers are formed. Using Nafion, stable films of the cation radical dimer or dication of 2,5'-bis(thiomethyl)terthiophene could be formed.

Introduction

The cation radicals and dications of oligothiophenes have become interesting as models for the polarons and bipolarons proposed to be present in oxidized polythiophene.¹ As reviewed in the two accompanying papers, polarons and bipolarons form the theoretical basis for understanding the conducting polymer, and it would be useful to have some spectroscopic handle to clarify their role in the structure and conductivity. Because unsubstituted oligothiophenes, such as terthiophene, polymerize upon oxidation and the larger oligomers are rather insoluble, it has only recently become possible to study the oxidized species. This was made possible by blocking the terminal positions to prevent, or at least slow down, the polymerization process. Thus, Tour, Diaz, and co-workers,² following Fichou and co-workers³ who studied unsubstituted sexithienyl, 1, have prepared a series of terminally blocked oligothiophene cation radicals, e.g., 2⁺, and dications by ferric chloride oxidation in methylene chloride, and recorded the vis-near-IR and ESR spectra. Caspar and co-workers have further stabilized the cations by incorporating them in zeolites.⁴ Again vis-near-IR spectra were recorded. Studies from this laboratory showed that terminally blocked terthiophenes could be oxidized to cation radicals and dications in acetonitrile.⁵ Because of the short lifetime of the ions in this solvent, the vis-near-IR spectra were recorded with spectroelectrochemistry and in situ ESR experiments were used.

Although cyclic voltammetry (CV) has provided definitive evidence^{2,5} for anodic formation of the cation radicals and dications as somewhat stable species, the spectroscopic results seem particularly important. The reported cation radical vis-near-IR spectra²⁻⁵ are, with one exception, in good agreement. Cation radicals in this series have a closely spaced pair of peaks in the vis and a second pair in the NIR. The bands for the substituted terthiophene

cation radicals are near 600 and 1100 nm. Longer oligomers show these bands at longer wavelength, e.g., sexithienyl cation radicals have bands near 800 and 1500 nm. Dications show only one closely spaced pair of bands; these appear near 600 nm for terthienyl and 1100 nm for sexithienyls. Although we have some concern about previous interpretations of the spectra in terms of polaron-bipolaron theory, it is theoretically reasonable that dications absorb at shorter wavelength than the cation radicals, and the results suggest that bipolarons should absorb at shorter wavelengths than polarons.

ESR studies²⁻⁵ are in agreement in that all the cation radicals show strong spectra in methylene chloride. There is, however, an unresolved question concerning the hyperfine coupling (or lack of it). In all cases the dications showed no ESR spectra as expected.

An observation of particular interest for the structure of oxidized polythiophene is that in acetonitrile solution the cation radicals form π -dimers.⁵ These otherwise unreported dimers were identified by optical and ESR spectra, as well as by changes in the CV. Because they are diamagnetic the π -dimers are interesting as alternatives to bipolarons.

We set out in the present investigation to solidify our understanding in this area and to develop a useful chemical method for the generation of oligothiophene cation radicals and dications. We report on a photooxidation method which, since it works well for small oligomers, should have

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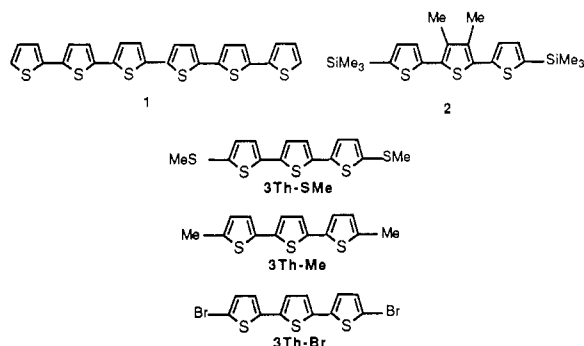
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wide applicability and avoid the potentially complicating presence of Fe (II and III) species in the solution. Because we had access to the manuscript of Tour and Diaz² when writing this paper, we are able to address several of the above questions with some certainty.

The photooxidation method described here has precedent in the photooxidation of oligothiophenes performed with organic electron acceptors. Because some oligothiophenes are pesticides, this has a rich history.⁶⁻¹⁰ Most recently this has been studied by transient visible spectroscopy by Scaiano and co-workers using acceptors such as tetracyanoethylene and methylviologen,^{11,12} who were able to detect the cation radicals of several terthiophenes. Here we use strong acids to catalyze photooxidation by oxygen. The use of strong acids to generate cation radicals is well-known in the ESR literature¹³ and there are several examples of acid-catalyzed photooxidations with oxygen as oxidant to form endoperoxides.¹⁴

Results and Discussion

Optical Spectra of Neutral Oligothiophenes. The substituted terthienyls, 2,5''-(dithiomethyl)-5,2',5',2''-terthienyl (3Th-SMe) and the 2,5''-dimethyl (3Th-Me) and -dibromo (3Th-Br) derivatives, exhibit absorption bands



at 384 ($\log \epsilon$ 4.42), 363 ($\log \epsilon$ 4.30), and 365 nm ($\log \epsilon$ 4.00), respectively. These bands, which are assigned to π - π^* transitions, are shifted bathochromically by 10–30 nm with respect to the unsubstituted terthienyl ($\lambda_{\max} = 355$ nm). The nonbonding π -electrons in the substituent, especially in 3Th-SMe, participate in the π -system and extend the conjugation.

These compounds emit light upon photoexcitation. The emission spectra of all the investigated terthienyls show the same fine structure; two overlapping peaks and a long-wavelength shoulder. The emission spectra of 3Th-Me and 3Th-Br are practically the same, with peaks at 424,

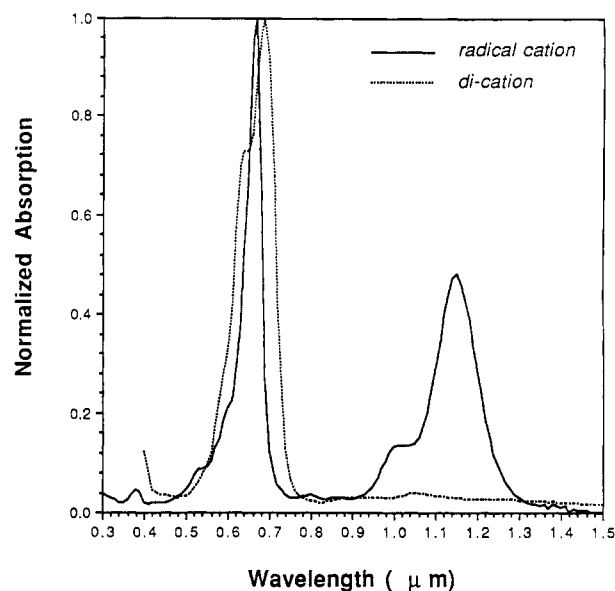


Figure 1. Spectra of 3Th-SMe⁺ (solid line) in MC/TFA and 3Th-SMe²⁺ (dashed line) in MSA.

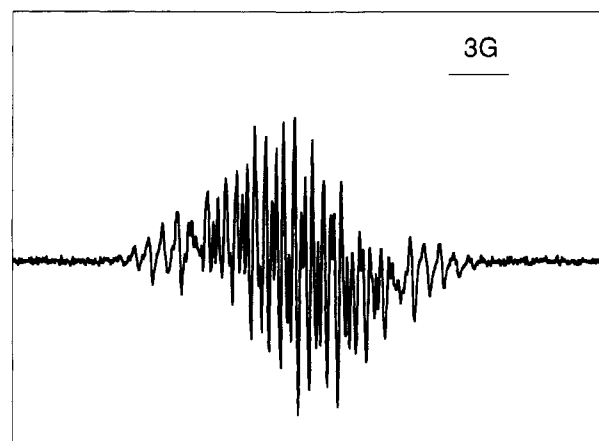


Figure 2. ESR spectrum of 3Th-SMe⁺ (A). Modulation amplitude 0.08 G.

448, and 473 nm. 3Th-SMe has the same bands shifted to longer wavelengths: 454, 478, and 510 nm. The energy differences between the peaks in each spectrum are 1100–1300 cm^{-1} , values which are typical for vibronic splitting. The emission quantum yields of 3Th-Me, 3Th-Br, and 3Th-SMe were 1, 2.6, and 8%, respectively.

Photooxidation of 3Th-SMe in Methylene Chloride. When 3Th-SMe was dissolved in a solution of methylene chloride/trifluoroacetic acid (20%, v:v, denoted MC/TFA) the color of the solution changed instantly from yellow to light green. Within 24 h in air, the color became dark green and finally a blue solution was obtained. The reaction was monitored by vis-near-IR spectroscopy which revealed that while the peak at 383 nm decreased two pairs of bands at 600, 665 and 1010, 1150 nm increased (Figure 1, solid line). The process was characterized by an isosbestic point at 445 nm. The optical and ESR spectra (Figure 2) of the new species were identical to those of the cation radical (3Th-SMe⁺), which had been prepared coulometrically.⁵ The vis-near-IR spectrum is quite similar to that for cation radical 2⁺ prepared with FeCl_3 .² In contrast to the spectrum in Figure 2, ESR spectra of FeCl_3 -generated oligothiophene cation radicals are single lines without evidence for hyperfine coupling. Although we have been able to approximately simulate the hyperfine coupling for 3Th-SMe⁺, we are not confident of the assignments. (A

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particular problem may be conformers.) We have, however, gained some understanding of the lack of hyperfine coupling in the ESR spectra of FeCl_3 generated cation radicals. When the 3Th-SMe⁺ solution of Figure 2 was treated with FeCl_3 , the hyperfine coupling disappeared to give a broad envelope similar to the previously observed spectrum. The peak-to-peak separation of the single line was 6.7 G, a value similar to that found for several other oligothiophene cation radicals generated using FeCl_3 .² This same spectrum resulted when 3Th-SMe was directly oxidized with FeCl_3 .

The rate of the oxidation process was enhanced dramatically when the solution was irradiated. For example, when a solution of 3Th-SMe was irradiated at 366 nm the rate of the reaction increased by 2 orders of magnitude in comparison to a sample that was exposed only to the light in the laboratory. Once a full conversion of 3Th-SMe to its cation radical was accomplished the spectrum of the latter was unchanged for many days when exposed to the light of the laboratory, indicating good stability of 3Th-SMe⁺. Assuming quantitative conversion, the extinction coefficient of 3Th-SMe⁺ at 665 nm ($\log \epsilon = 4.95$) was found to be larger than that of the neutral compound.

At this point it was important to examine the factors that influence the oxidation process. Three solutions with the same concentration of 3Th-SMe were prepared in the dark. Two solutions, I and II, were composed of MC/TFA (10.45%). To a control solution, III, no TFA was added. The solutions were kept 4 min in the dark, and then solution I and III were exposed to the radiation source. II was kept in the dark throughout the experiment. The oxidation was carried out in quartz cells, and the spectra of all the solutions were taken in the same time intervals. Only solution I was reactive, where reaction was complete in <10 min. It is concluded that this is a *photochemical* oxidation and that a *proton source is essential for the formation of the cation radical*.

The oxidation of 3Th-SMe in the presence of some other acids was also investigated. In a mixture of MC/acetic acid, or even in glacial acetic acid, formation of 3Th-SMe⁺ was *not* observed even when photolyzed for 40 min. Dinitrobenzene sulfonic acid, pure TFA and mixtures of MC/5–30% methanesulfonic acid were found to be suitable proton sources for the formation of 3Th-SMe⁺. When 3Th-SMe was dissolved in pure methanesulfonic acid (99%) or sulfuric acid (96%), a blue solution was obtained immediately, but the spectra had a strong absorption band at 688 nm ($\log \epsilon = 4.738$) and a shoulder at 625 nm. There were no absorption bands beyond 700 nm (Figure 1, dashed line), and this blue solution did not have any ESR signal. As previously established by spectroelectrochemical studies,⁵ this is the dication, 3Th-SMe²⁺. Thus, these stronger acids push the reaction beyond the cation radical. 3Th-SMe²⁺ is stable in these solvents for many days.

It seemed likely that molecular oxygen was acting as an oxidant in the above reactions, so to test this hypothesis, the following experiment was performed. Dichloroethane, which is less volatile than CH_2Cl_2 , and TFA were degassed for 10 h in a Dri Lab glovebox filled with dry argon, and a solution of 3Th-SMe (0.41 mM) in dichloroethane/TFA (10%) was prepared in a quartz cell. The sealed cell was illuminated at 360 nm. The control reaction was carried out in the atmosphere. In the presence of oxygen the concentration of 3Th-SMe diminished during the photochemical process and the reaction was completed after ca. 50 min of radiation. When the reaction was carried out under Ar, there was a small initial reaction, but after 3 min

the slope dA/dt was close to zero. The spectrum did not change after 48 h. Although TFA could be indirectly involved in this reaction,¹⁵ we feel confident that oxygen is the oxidant, and it is active only in the presence of strong acids.

It is now well established that the lowest triplet state of α -terthienyl and its analogs are excellent singlet oxygen sensitizers^{9,10} and that formation of 3Th^{•+} and $\text{O}_2^{\cdot-}$ by electron transfer to O_2 is a minor process.¹² We suggest, however, that if the $\text{O}_2^{\cdot-}$ is trapped by acid this minor pathway provides an irreversible route to the cation radical formation observed here. Although we have not elucidated the mechanism, we do note that the pK_b of $\text{O}_2^{\cdot-}$, 4.88,¹⁶ is such that it might be more slowly protonated by acetic than trifluoroacetic acid. Because the $\text{O}_2^{\cdot-}$ will reduce 3Th-SMe⁺, a rapid protonation step is required. Indeed it was found that the rate of the reaction increased with the concentration of TFA in the solution.

Photooxidation of 3Th-SMe in Acetonitrile. Spectroelectrochemical oxidation of 3Th-SMe in CH_3CN –0.1 M tetrabutylammonium fluoroborate yield complex UV–vis–near-IR spectra. These spectra were attributed to the presence of both monomer and dimer cation radical.⁵ Since we developed a simple method to produce 3Th-SMe⁺, it was of interest to investigate the behavior of this species in CH_3CN .

A solution of 3Th-SMe (0.62 mM) in CH_3CN /TFA (15%) was photolyzed at room temperature, and the progress of the reaction was monitored spectrally. The peak at 383 nm (3Th-SMe) decreased, and four peaks, at 526, 665, 836, and 1150 nm, grew during the reaction. The band at 1150 nm was accompanied by a shoulder at shorter wavelength. Following our previous results the bands at 665 and near 1150 nm are attributed to 3Th-SMe⁺ (monomer), while the absorptions at 525 and 836 nm and near 1150 nm are ascribed to the cation radical π -dimer, (3Th-SMe⁺)₂.

To investigate the monomer–dimer equilibrium, the reaction mixture was diluted sequentially and the spectra were recorded. This dilution was carried out five times, finally reaching dilution by a factor of 32. Upon dilution the equilibrium is expected to shift toward the monomer (eq 1). Indeed, it was found that for the most dilute solution the absorption bands at 525 and 836 nm disappeared. The absorption (A) at 383 (due to neutral), 526, 665, and 836 nm was plotted vs the concentration (C). The A_{383} vs C plot was linear with intercept close to zero, as expected from Beer's law. A_{665} vs C gave a curve which exhibited a positive deviation from Beer's law, whereas both A_{835} vs C and A_{525} vs C curves deviated negatively. The Beer's law plots are inserted in Figure 3. This behavior is typical of a monomer–dimer equilibrium.

These experiments enable a calculation of the monomer–dimer equilibrium constant (K_{eq}). The extinction coefficient of 3Th-SMe in CH_3CN was found to be $\log \epsilon = 4.35$. The extinction coefficient of 3Th-SMe⁺ at 665 nm, calculated from the most dilute solution where the

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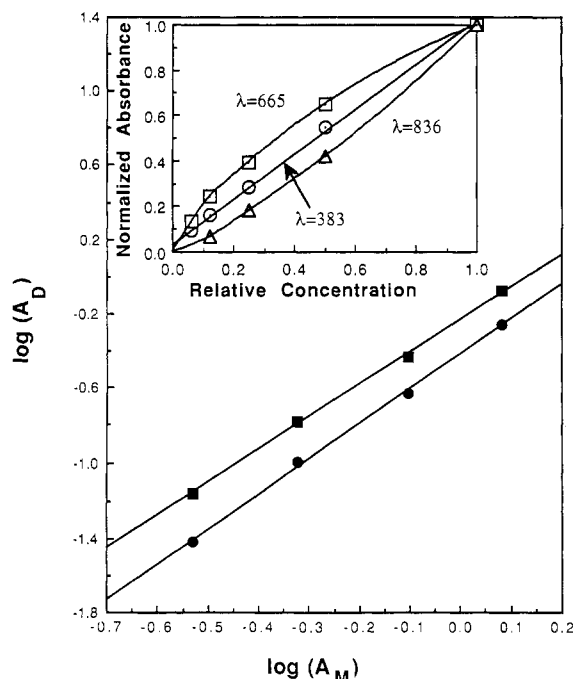
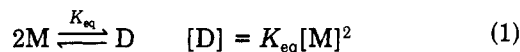


Figure 3. log-log plot of the 3Th-SMe²⁺ absorption (A_M) and the 3Th-SMe₂²⁺ absorption (A_D). Inserted: Beer's law at 383, 665, and 836 nm.

π -dimer is absent, is $\log \epsilon = 4.88$. By difference the π -dimer at 836 nm has $\log \epsilon = 4.36$. The concentration of all the participants at any dilution was calculated and substitution of the concentrations of the monomer [M] and the π -dimer [D] in eq 3 gave a value of $K_{eq} = (1.00 \pm 0.05) \times 10^4 \text{ M}^{-1}$ for all the dilutions. We note that this value is substantially larger than the 250 M^{-1} value determined for 3Th-Me:^{5a}



therefore

$$\log A_D = \log [\epsilon_D/\epsilon_M^2 I] + \log K_{eq} + 2 \log A_M \quad (2)$$

where I is the optical path and ϵ_D and ϵ_M are the extinction coefficients of the dimer and monomer, respectively.

A log-log plot of the absorption of the dimer vs the absorption of the monomer (A_D and A_M , respectively) should be linear with slope equal to 2. Experimentally we found slope of 1.83 (Figure 3).

The results obtained in CH₃CN solvent confirm the conclusions from spectroelectrochemical experiments.⁵ Now it is also clear that π -dimers form at room temperature and millimolar concentrations in CH₃CN but not in MC because a more polar solvent is needed to solvate the dicationic π -dimer. On the other hand the equilibrium constant in CH₃CN is higher than for other examples of ion radical dimers, and it seemed possible that we might detect the dimer at low temperature in MC. Indeed, when a solution of 3Th-SMe²⁺ in MC/TFA was cooled to ~ -20 °C, bands at 530, 835, and 1020 nm due to (3Th-SMe²⁺)₂ were obtained superimposed on the absorption bands of 3Th-SMe²⁺.

Photooxidation of 3Th-Me and 3Th-Br. A blue solution was obtained when 3Th-Me was dissolved in MC/TFA. As expected from its more positive E° , the oxidation of 3Th-Me was slower than the oxidation of the 3Th-SMe. The spectrum of the oxidized product consisted of a closely spaced pair of peaks at 580 and 555 nm and another peak at 890 nm. This spectrum agrees well with the spectrum of the electrochemically prepared 3Th-Me²⁺

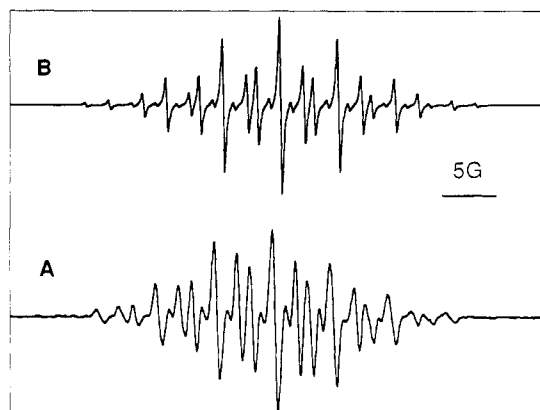


Figure 4. ESR spectrum of 3T-Me²⁺: (A) experimental spectrum (modulation amplitude 0.5 G; power 13 dB); (B) simulated spectrum made of two species with the ratio of 7:1.

in CH₃CN but contradicts the recently reported spectrum of this cation radical in the zeolite Na- β , which shows a single peak at 580 nm with no absorption at longer wavelength.⁴ The stability of 3Th-Me²⁺ was less than that of 3Th-SMe²⁺, but it was stable for several days.

The ESR spectrum of 3T-Me²⁺ prepared by photooxidation is shown in Figure 4A. Attempts to simulate this spectrum assuming it arises from a single radical species were unsuccessful. However, the experimental spectrum could be simulated when two radical species with similar g factors and different abundance were assumed (Figure 4B). The more abundant species (86%) has hyperfine splitting constants of $a_H(6H) = 5.3 \text{ G}$ and $a_H(2H) = 2.18 \text{ G}$, while the less abundant species (14%) has hyperfine splitting constants of $a_H(6H) = 5.3 \text{ G}$ and $a_H(2H) = 0.95 \text{ G}$. The hyperfine splitting constants of the two other sets of equivalent protons are too small to be detected ($<0.05 \text{ G}$). This interpretation is similar to that made to explain the spectrum of α -terthienyl cation radical.¹⁹ In that case the spectral pattern was analyzed as arising from the superimposition of two rotamers having different hyperfine splitting. The more abundant species (67%) was assigned to the trans-trans isomer, while the less abundant species (33%) was assigned to the trans-cis isomer. The hyperfine splitting constants of the relevant protons were ca. 2, 3.4, and $<0.15 \text{ G}$.

Attempts to form the cation radical in CH₃CN were not as successful. When a solution of 3Th-Me in CH₃CN/TFA was photolyzed ($\lambda = 366 \text{ nm}$), the band at 570 nm increased initially but after ca. 8 min it decreased. The band at 890 nm was masked by a broad absorption band at 734 nm. When the solution was diluted as described above, the absorption at 734 nm decreased linearly; thus, the band at 734 nm is ascribed to decomposition product(s) and not to the π -dimer. This conclusion is further supported by the absence of a band at $\sim 470 \text{ nm}$ for the dimer in CH₃CN.^{5a} Similar cation radical instability was found in electrochemical oxidations in CH₃CN.⁵

The better stability of the oxidized species of 3Th-SMe in comparison to 3Th-Me presumably arises because the thiomethyl substituent can stabilize the positive charge(s) better than the methyl due to its nonbonding π electrons which increase the conjugation length.

3Th-Br is oxidized at higher potential (1.19 V) than 3Th-SMe (0.89 V). Electrochemical oxidation of 3Th-Br in CH₃CN, Bu₄NBF₄ gave broad CV peaks. When 3Th-Br was dissolved in MC/TFA (10%) and irradiated at room

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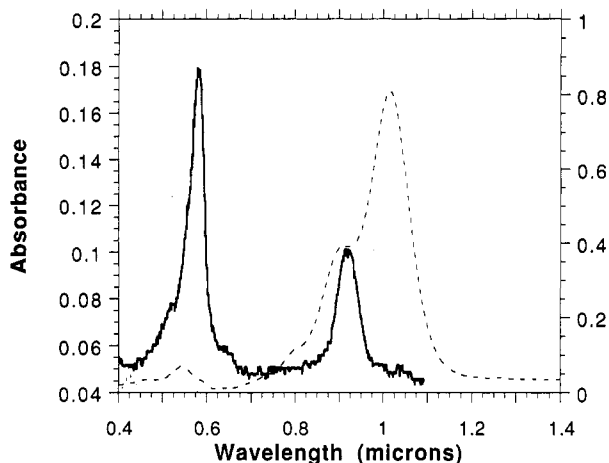
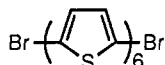


Figure 5. Spectra of 3Th-Br in (a) TFA (b) MSA.

temperature, there was little reaction even after 90 min. A higher concentration of TFA, ca. 50%, caused an increase in the rate of the process and the solution became colored within a few minutes. Typical bands for the cation radical species were observed at 581 and 914 nm. The cation radical is very unstable; under 366-nm illumination or even in the artificial light of the laboratory, several other bands grew in with time. The decomposition of the cation radical was minimized in pure TFA. A saturated solution of 0.4 mg of 3Th-Br in 2 mL of TFA was prepared and filtered. After 15 min of irradiation, the typical cation radical spectrum (Figure 5) was obtained. It was stable for ca. 20 min. after which a band at 1030 nm was observed.

When MSA was used as the solvent, an absorption at 1015 nm accompanied with a shoulder at 898 nm was observed (Figure 5). The solution did not have an ESR signal. On the basis of the above results, this band cannot be attributed to a terthienyl derivative because the dication band of the investigated terthienyls is within ± 0.13 eV of the short-wavelength band of the cation radical. Specifically, electrochemically prepared 3Th-Br²⁺ at -35 °C shows a band at 650 nm and a shoulder at 608 nm. A reasonable explanation for the spectrum shown in Figure 5 is that the terminal dibromo-substituted sexithienyl dication (6Th-Br²⁺) was formed via σ -dimerization and loss of two bromines.¹⁷ The position and structure of this band are identical to that of the sexithienyl dication reported by Fichou.³



6Th-Br

Incorporation of Oxidized 3Th-SMe in Nafion. Nafion has been used as a superacid catalyst for a wide variety of reactions.¹⁸ It was, therefore, interesting to see if this perfluorinated ion-exchange membrane with pendant sulfonic acid groups, could be used as a proton source for the photooxidation. It was expected that the positively charged thiophene species would be incorporated into the negatively charged sulfonate membrane.

When a piece of acidic Nafion was placed in MC containing 3Th-SMe, no reaction took place even when the solution was illuminated for 60 min. This is probably because the hydrophilic membrane was not swollen in this nonpolar solvent. Indeed, when CH₃CN, which has a much higher dielectric constant, was used, the color of the membrane changed within a few minutes in the artificial light of the laboratory. The surrounding solution, which

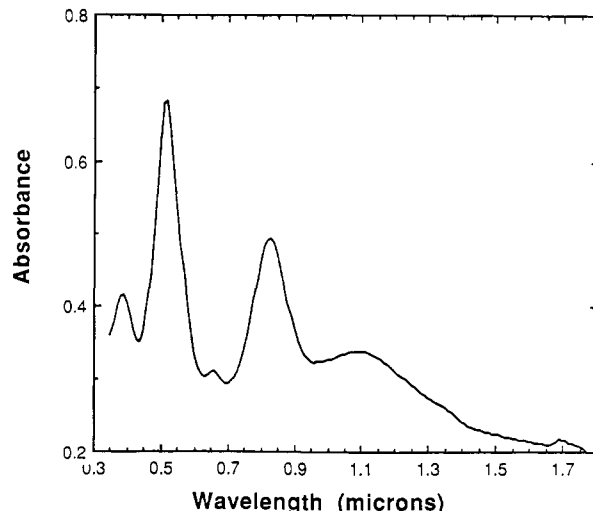
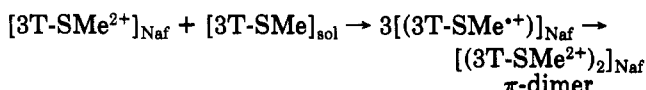


Figure 6. Spectrum of (3Th-SMe)₂²⁺ incorporated in Nafion.

contains no TFA, was uncolored. The vis-NIR spectrum of the film showed two relatively narrow peaks at 519 and 829 nm and a smaller and broader peak at 1100 nm (Figure 6). This spectrum is assigned to the π -dimer, (3Th-SMe⁺)₂, which appears to be incorporated homogeneously in the membrane. The spectrum did not change during several days when stored in the atmosphere.

When Nafion was placed in a solution of 3Th-SMe in MC/TFA (10%), a different species was found in the membrane. The spectrum of the homogeneously colored, blue film indicated that the dication 3Th-SMe²⁺ was incorporated in the film. In this solvent mixture only 3Th-SMe⁺ is formed in the absence of Nafion. This finding shows that the acidity of Nafion is high enough to allow oxidation of the cation radical to the dication.

Comparing the different results for the two solvents, we suggest that 3Th-SMe²⁺ is initially formed inside the film and the difference in the final loaded species results from the different oxidation state of 3Th-SMe in the solution. In acetonitrile, neutral 3Th-SMe is in the solution and reacts with the dication in the film to form the cation radical (comproportionation) which is then dimerized in the film due to its high concentration. When MC/TFA is used as solvent, 3Th-SMe⁺ is present in the solution and the comproportionation does not take place in the film:

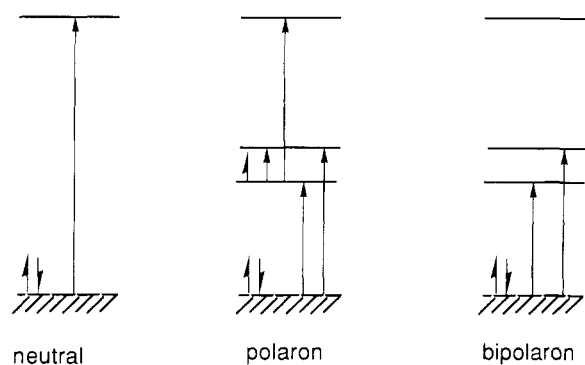


Conclusions and Theoretical Interpretations

It has been demonstrated here that terthiophenes can be photooxidized to cation radicals with the system MC/TFA/O₂. The reaction involves oxygen as oxidant and can be catalyzed by a variety of strong acids. In more acidic media dications are formed. In CH₃CN the cation radicals π -dimerize. The spectra are completely consistent with those measured for electrochemical or FeCl₃ generated cations.

Previously, the spectra of oligothiophene cation radicals and dications have been interpreted with polaron-bipolaron theory.^{2-4,20} As applied, this theory predicts four bands for cation radicals and two bands for dications^{3a} (Scheme I). Taking the dications first, we note that there are often two closely spaced (about 0.2 eV) peaks in the visible spectra^{2,3,5} but that these can be logically assigned

Scheme I. Polaron-Bipolaron Description



to the vibrational structure of one $\pi-\pi^*$ band (conformers are also possible). Many spectra of aromatic compounds, including the emission spectra of the neutral terthiophenes, show $\pi-\pi^*$ vibrational splitting of this magnitude.^{21,22} Polaron-bipolaron theory, which is qualitative, can only explain the appearance of two closely spaced peaks if the two states in the gap are very closely spaced (Scheme I). This, however, suggests that the bands should be at about one-half the $\pi-\pi^*$ transition energy, thus occurring at much longer wavelengths than observed. It is also unreasonable that the splitting should be 0.2 eV for all the oligomers studied, which have transition energies that vary from 2.5 to 1 eV. It is concluded that dication spectra are better explained by vibrational splitting of a single $\pi-\pi^*$ band than by two electronic transitions required by polaron-bipolaron theory.

Turning to cation radicals, the experimental spectra for oligomers from 3Th to 8Th show two bands, each with this same small 0.2-eV (1400 cm^{-1}) splitting.² A polaron description would assign these four peaks to four different electronic transitions. It is unreasonable, however, that all the cation radicals investigated would accidentally have this 0.2-eV splitting between transitions. Indeed, Scheme I shows that there might be two closely spaced electronic transitions but not two *pairs* of closely spaced electronic transitions. Again, polaron-bipolaron theory with four different electronic transitions does not explain the results, as well as an orbital theory with two electronic transitions each split vibrationally.

The polaron-bipolaron theory is, of course, inappropriate for oligomers because the oligomers do not have a band structure. Molecular orbital calculations provide the proper approach and quantitative results. We have done PPP calculations, known to be useful for the prediction of optical spectra, on terthiophene dication. These cal-

culations show that the dication should have one band. The agreement with experiment is more than satisfactory in that the band position is accurate to within 30 nm. A more extensive and careful treatment of the theoretical description of the ions is in progress.

Finally, we turn to the question of bipolarons in oxidized polythiophenes. Although it has been claimed that bipolarons are dominant in certain polythiophenes,²³ this is still controversial.²⁴ Important experimental evidence cited in favor of these species is the low ESR spin count found in several cases.²³ It was logically reasoned that two paramagnetic polarons along one chain could react to form diamagnetic bipolarons. We present the alternative view that two polarons can form diamagnetic π -dimers between chains, which are responsible for low spin counts.

This bipolaron vs π -dimer issue might be addressed by a careful consideration of the optical spectra of low-spin oxidized polythiophenes. Starting from model oligomers is risky because the appropriate data, for example, spectra of solid salts of oxidized oligomers, is not yet available. We do point out that the longest wavelength band of a cation radical π -dimer is at an energy similar to that of its monomer. We expect then that π -dimers of polarons will absorb at NIR wavelengths appropriate for oxidized low-spin polythiophene.²³ Again, these interchain π -interactions, which are reasonably expected, can comply with the experimental observations. We think π -dimers deserve more attention.

Experimental Section

The oligothiophene syntheses have been reported.⁵ Instruments used for ESR and optical spectroscopy have been described.⁵ Acetonitrile and methylene chloride (Burdick and Jackson) and trifluoroacetic acid and methanesulfonic acid (Aldrich) were used without further purification.

Photolyses were performed in 1-mm path-length quartz cells in air except where noted. Two mercury lamps were used: a Westinghouse 175-W low-pressure lamp, filtered through 5 cm of water to remove the IR and a 21-W UVSL 58, multiband UV lamp (Ultraviolet Production Inc., San Gabriel, CA).

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