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Mechanism of Photoinduced Step Polymerization of Thiophene by Onium Salts: Reactions of Phenyliodinium and Diphenylsulfinium Radical Cations with Thiophene

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ABSTRACT: Laser flash photolysis and EPR studies were performed to elucidate the mechanism of photoinduced step polymerization of thiophene by using diphenyliodonium (Ph_2I^+) and triphenylsulphonium (Ph_3S^+) ions as photoinitiators. Photoexcitation of these ions generated phenyliodinium ($PhI^{\bullet+}$) and diphenylsulphinium ($Ph_2S^{\bullet+}$) radical cations, which were readily quenched by thiophene with rate constants of $k_q = 1.26 \times 10^{10}$ and 1.7×10^5 M^{-1} s^{-1}, respectively. The transient absorption spectra of the corresponding thiophene radical cations were not directly detectable because of the spectral overlap with the precursor salts. However, the related electron-transfer reaction was confirmed by quenching of the $PhI^{\bullet+}$ radical cation with bithiophene to form the radical cation of bithiophene, which absorb strongly at 420 nm. EPR studies also confirmed the proposed electron-transfer mechanism through the direct detection of the radical cation of thiophene.

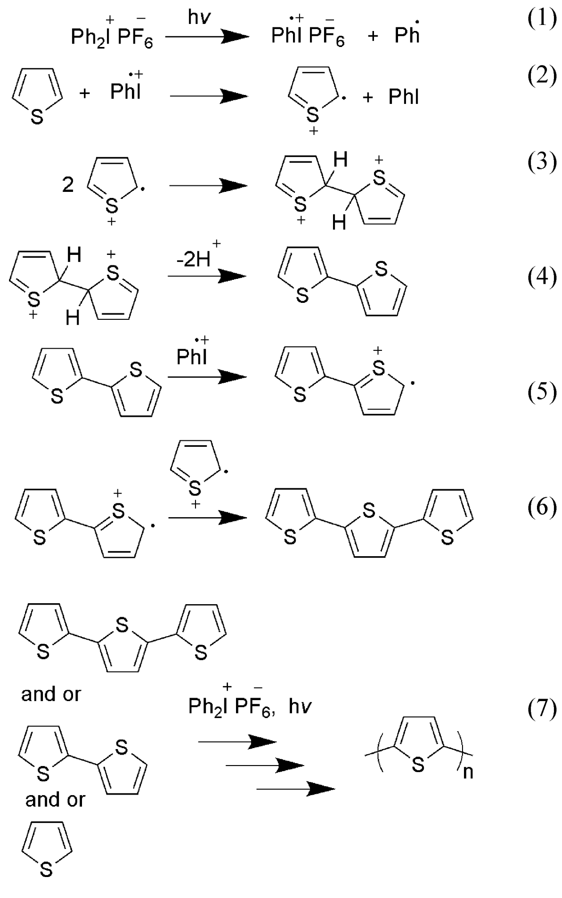
Introduction

Thin organic films of conjugated polymers have attracted great interest due to their promising potential for electronics and electro-optic devices.[1] Polythiophenes are one of the most extensively studied families of conjugated polymers because of their characteristic electronic and optical properties.[2−10] Usually, polythiophenes are obtained by chemical or electrochemical polymerization processes, which provides films with different morphologies and consequently slightly different physical and chemical properties.

Recently, we have shown[11] that polythiophenes can also be obtained by means of UV irradiation of thiophene in the presence a diphenyliodonium salt. Alkoxylpyridinium and triphenylsulfonium salts were also found to facilitate the polymerization of thiophene. The polymerization is accompanied by the formation of a polymer film on the surface of the reaction vessel surface. The polymerization mechanism involving electron transfer from photochemically generated phenyliodinium radical cations to thiophene that was proposed is shown in eqs 1−7 of Scheme 1.[11]

These investigations did not answer the question whether the radical cations $PhI^{\bullet+}$, formed according to eq 1, react directly with thiophene and whether thiophene radical cations formed in this way start the polymerization. Also, other polymerization mechanisms may prevail. Therefore, laser flash photolysis studies with diphenyliodonium and triphenylsulfonium salts in the presence of thiophene were performed in order to provide information that would be useful in confirming the validity of the proposed mechanism (eqs 1−7).

Scheme 1



Experimental Section

Diphenyliodonium hexafluorophosphate, triphenylsulfonium hexafluorophosphate, and acetonitrile (Aldrich) were used as received.

Laser flash photolysis experiments (time-resolved UV spectroscopy) employed the pulses from an excimer laser (Lextra 50, Lambda Physik, ca. 50 mJ/pulse, 15 ns pulse width). A pulsed 150 W xenon lamp combined with an ISA H20 monochromator serves as the monitoring system. The signals from a Hamamatsu R928 photomultiplier tube were terminated into 50 ohm and stored in a Tektronix TDS 380 (400 MHz bandwidth) programmable digitizer. This digitizer was controlled along with other aspects of the

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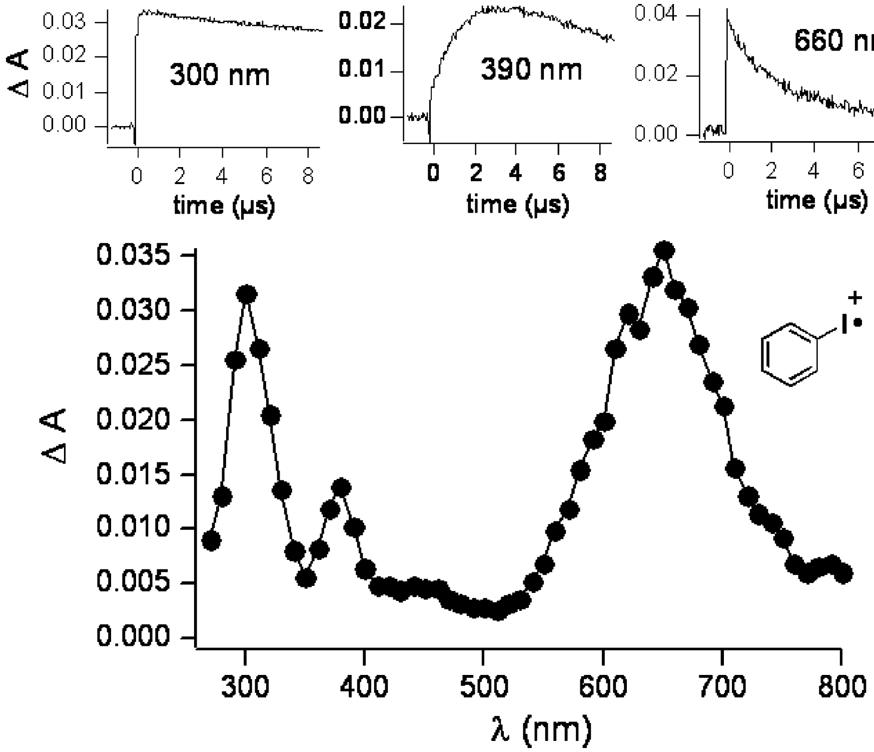


Figure 1. Transient optical absorption spectrum recorded 0−1.5 μs following laser excitation (308 nm; 20 mJ/pulse) of $Ph_2I^+PF_6^-$ in argon-saturated acetonitrile solution at 23 °C. The insets show the kinetic traces at 300, 390, and 690 nm.

experiment (laser trigger, shutters, lamp pulser, monochromator, etc.) through a GPIB interface board (National Instruments NBG-PIB) using a Macintosh G3 with Labview 5 software (National Instruments). Further details were described earlier.[17] Kinetic traces were monitored at specific wavelengths, and the absorption spectra at various delay times and integration time windows were reconstructed from these traces. Solutions of diphenyliodonium hexafluorophosphate and triphenylsulfonium hexafluorophosphate in acetonitrile were prepared at concentrations such that the absorbance was ~0.3 at the excitation wavelength (308 nm). Transient absorption spectra were recorded employing a Suprasil quartz flow cell (1 × 1 cm) to ensure that a fresh volume of sample was irradiated in each laser pulse. Quenching rate constants were measured using static samples (4 mL) contained in 1 × 1 cm Suprasil quartz cells. Fresh solutions were prepared for each quencher concentration.

EPR measurements were performed at room temperature on a Bruker EMX spectrometer operating at X-band (9.5 GHz). Air-saturated acetonitrile solutions of $Ph_2I^+PF_6^-$ and thiophene were flowed through the cavity of the EPR spectrometer and were irradiated with a 300 W Xe lamp (ILC Technology, Inc.).

Results and Discussion

Irradiation of $Ph_2I^+PF_6^-$ and $Ph_3S^+PF_6^-$ in acetonitrile solution with laser pulses of 308 nm (~15 ns pulse width) results in the formation of transients, assigned to $PhI^{•+}$ and $Ph_2S^{•+}$, respectively (Figures 1 and 2) based on previously published spectra.[12−14] The transient absorptions (660 nm for $PhI^{•+}$ and 740 nm for $Ph_2S^{•+}$) were used to determine the quenching rate constants (k_q) with thiophene by pseudo-first-order treatment (Figure 3).

The quenching rate constants determined in this work are compiled in Table 1. For comparison, this table also contains rate constants for quenching of $PhI^{•+}$ and $Ph_2S^{•+}$ by some representative aromatic compounds with electron-donating substituents.

As can be seen, $PhI^{•+}$ is quenched by thiophene with a high rate constant ($k_q = 1.26 \times 10^{10}$ M^{-1} s^{-1}) which is in the same order of magnitude as found for other aromatic quenchers possessing electron-donating substituents.[14] Thiophene is a parent aromatic molecule and does not possesses an electron-donating or electron-withdrawing substituent. The high reactivity observed for thiophene may be associated with the lone electron pairs at the S atom of the thiophene molecule. Thus, thiophene may act as an electron donor molecule due to the its polarizable π system.

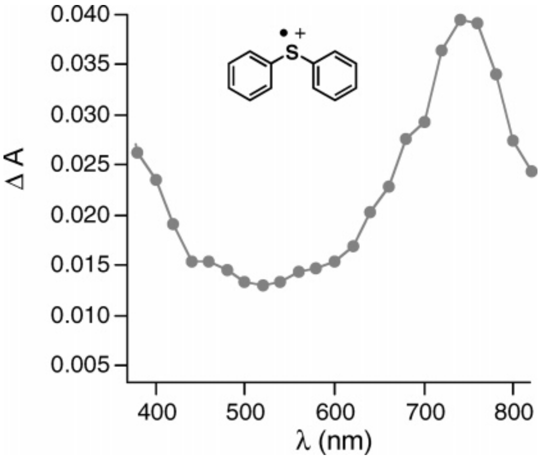


Figure 2. Transient optical absorption spectrum recorded 4.5−8.5 μs following laser excitation (308 nm) of $Ph_3S^+PF_6^-$ in argon-saturated acetonitrile solution at 23 °C.

The rate constant of quenching of sulfinium radical cations with thiophene is much smaller ($k_q = 1.7 \times 10^5$ M^{-1} s^{-1}) than for iodinium radical cations. This smaller rate constant is consistent with polymerization rates, where a much smaller rate of thiophene polymerization was observed for photoinitiation with $Ph_3S^+PF_6^-$ compared to $Ph_2I^+PF_6^-$.[11] The lower reactivity can be explained in terms of the quite different redox potentials (relative to SCE) of the two precursor ions: −1.2 V (Ph_3S^+)[15]

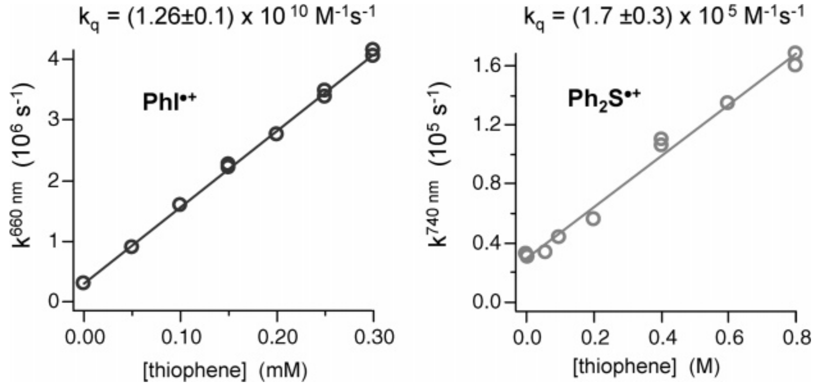


Figure 3. Reaction of thiophene with $PhI^{\bullet +}$ (left) and $Ph_2S^{\bullet +}$ (right) in acetonitrile solutions at 23 °C. Dependence of the pseudo-first-order rate constant of the decay of the optical absorption at 660 nm (left) and 740 nm (right) on the thiophene concentration after laser excitation (308 nm).

Table 1. Quenching Rate Constans (k_q) of the Radical Cations, $PhI^{\bullet +}$ and $Ph_2S^{\bullet +}$, with Thiophene and Some Selected Aromatic Compounds

	k_q (M^{-1} s^{-1})		
compound	$PhI^{\bullet +}$	$Ph_2S^{\bullet +}$	reference
thiophene	1.26×10^{10}	1.7×10^5	this work
methoxybenzene	1.10×10^{10}	6.8×10^6	14
phenol	1.10×10^{10}	3.50×10^7	14
1,2,3-trimethoxybenzene	1.20×10^{10}	1.20×10^{10}	14

and −0.2 V (Ph_2I^+),[16] i.e., the much higher oxidizing ability of Ph_2I^+.

The proposed mechanism (eqs 1−7) involves several intermediates, such as the thiophene radical cation and higher thiophene radical cations. The absorption spectra of these thiophene radical cations are known.[18] However, no new transient absorptions were detected under our experimental conditions because of the following reasons. Thiophene radical cations are known to show a transient absorption below 300 nm,[18] a spectral region which is not accessible under our experimental conditions due to the strong absorption of the iodonium salt itself. Oligomeric thiophene cation radicals such as the bithiophene cation radical are generated in secondary reaction steps (eq 5), which are not likely to be observable under our experimental conditions, since fresh solutions are flown into the sample cell before each laser pulse. However, the reaction in eq 5 can be directly investigated in laser flash photolysis experiments, where $Ph_2I^+PF_6^-$ is photolyzed in the presence of bithiophene. A strong transient absorption of bithiophene cation radicals was observed at 420 nm (Figure 4).

The assignment of the transient absorption to the bithiophene radical cation is in agreement with previously published spectra.[18,19] It should be pointed out that the laser power was only 32% compared to the experiments presented in Figure 1 because of the strong transient absorption. The kinetics of the

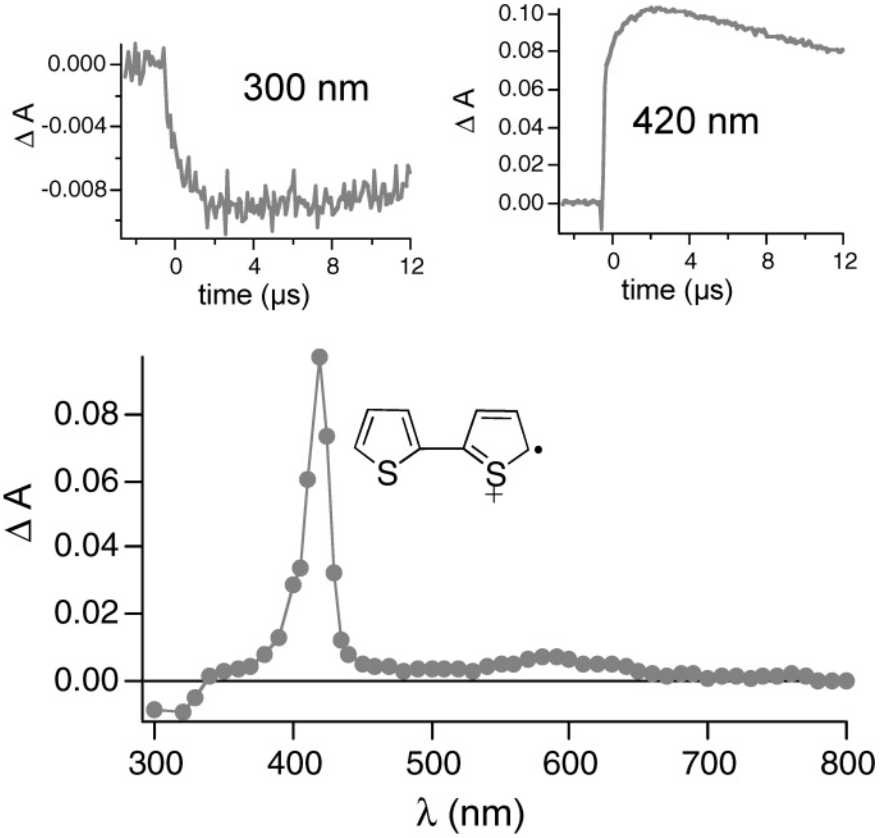


Figure 4. Transient optical absorption spectrum recorded 3−8 μs following laser excitation (308 nm; 6.4 mJ/pulse) of $Ph_2I^+PF_6^-$ in the presence of bithiophene (0.05 mM) in air-saturated acetonitrile solution at 23 °C. The insets show the kinetic traces at 300 and 420 nm.

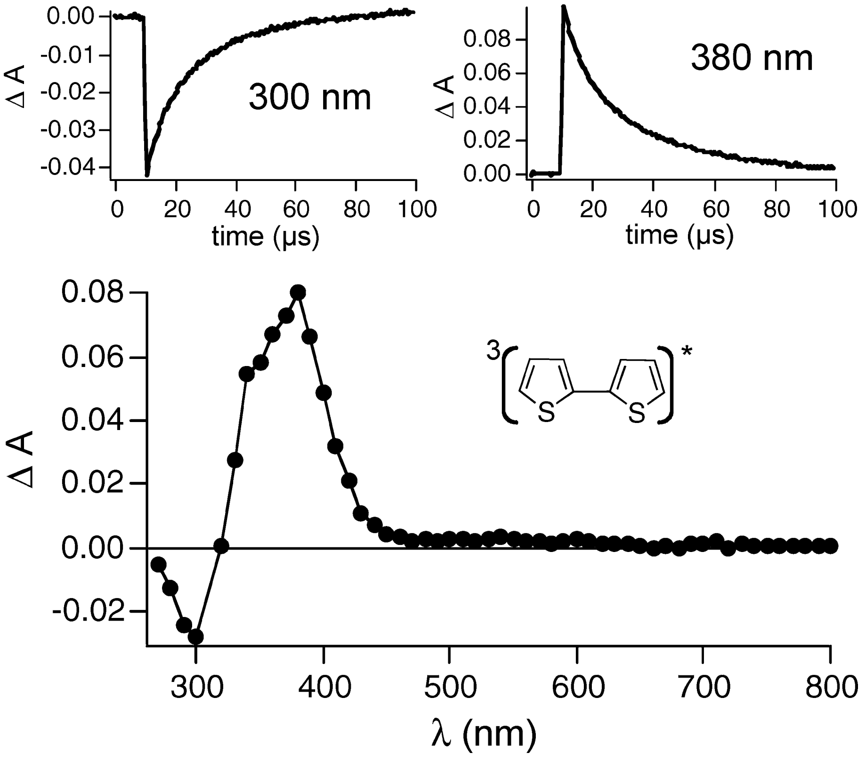
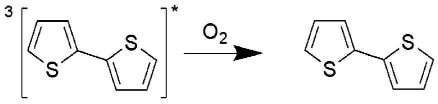


Figure 5. Transient optical absorption spectrum recorded 1−8 μs following laser excitation (308 nm; 6.4 mJ/pulse) of bithiophene (0.05 mM) in argon-saturated acetonitrile solution at 23 °C. The insets show the kinetic traces at 300 and 380 nm.

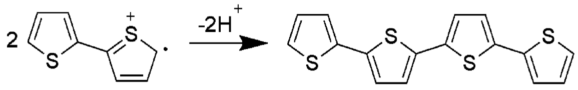
rise of the transient absorption at 420 nm is mixed. An instant rise (within the laser pulse) is followed by a slow rise. The slow rise is consistent with the desired formation of bithiophene cation radicals by the reaction of $PhI^{\bullet +}$ with bithiophene (eq 5). The fast rise is probably derived from an undesired transient, the formation of bithiophene triplets from direct excitation of bithiophene with 308 nm laser pulses. Bithiophene shows some absorbance at 308 nm. This was demonstrated in laser flash photolysis experiments of bithiophene in the absence of $Ph_2I^+PF_6^-$ with 308 nm laser pulses in argon-saturated acetonitrile solutions. Figure 5 shows the triplet−triplet absorption spectrum of bithiophene, which is in agreement with previously published spectra.[19] However, in air-saturated solutions, the bithiophene triplets get quenched rapidly (eq 8) (Figure 6, blue trace) and does not interfere with the kinetics of $PhI^{\bullet +}$ (Figure 6, red trace) at longer time scales (>1 μs).



(8)

In the presence of the photoinitiator, $Ph_2I^+PF_6^-$, $PhI^{\bullet +}$ radical cations were readily quenched by bithiophene (Figure 7) with a rate constant ($k_q = 1.2 \times 10^{10}$ M^{-1} s^{-1}) similar to that of thiophene and the true transient absorption of bithiophene radical cations formed according to the eq 5 can be observed after ~1 μs following the laser pulse (Figure 6, blue trace).

To investigate the proposed recombination of two bithiophene cation radicals (eq 9), laser flash photolysis experiments were performed at different laser power.



(9)

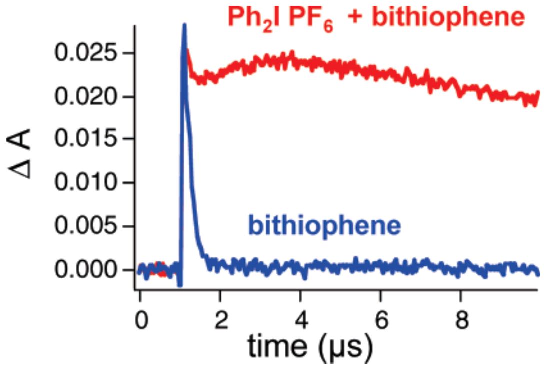


Figure 6. Kinetic traces recorded at 410 nm after irradiation with laser pulses (308 nm, 6.4 mJ/pulse) of air-saturated bithiophene solution (0.05 mM) in acetonitrile in the absence (blue) and presence of $Ph_2I^+PF_6^-$ (red).

At 100% laser power (more bithiophene cation radicals are generated) the decay of the bithiophene cation radicals is

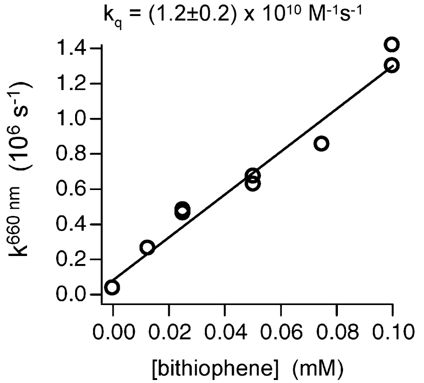


Figure 7. Reaction of bithiophene with $PhI^{\bullet +}$ in acetonitrile solutions at 23 °C. Dependence of the pseudo-first-order rate constant of the decay of the optical absorption at 660 nm on the bithiophene concentration after laser excitation (308 nm).

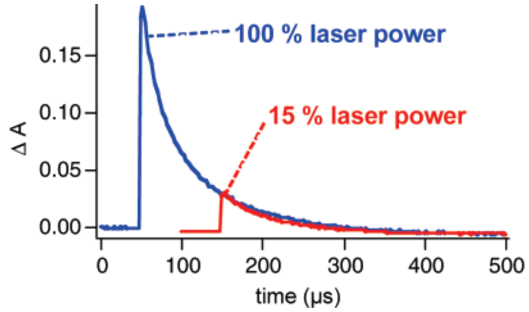


Figure 8. Dependence of the laser power on the decay kinetics of the transient at 410 nm formed from the irradiation of the air-saturated acetonitrile solution of $Ph_2I^+PF_6^-$ in the presence of bithiophene (0.05 mM) with laser pulses (308 nm; 20 mJ/pulse).

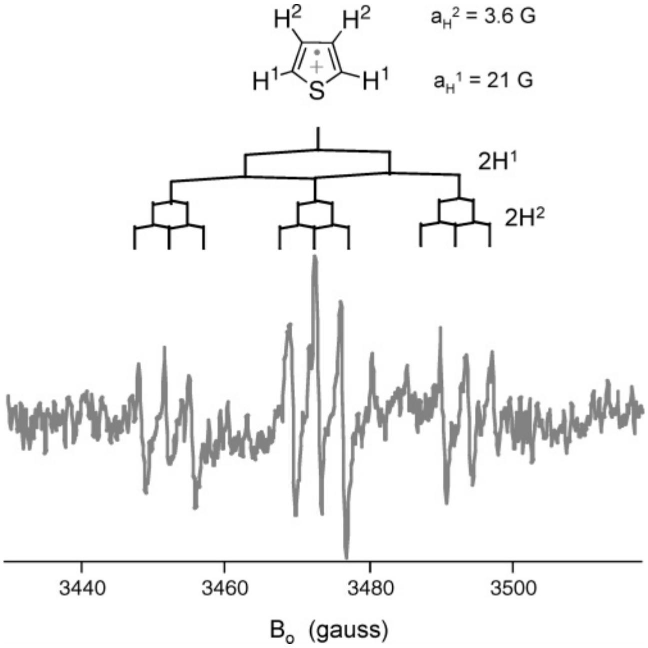


Figure 9. EPR spectrum of thiophene radical cation formed during the irradiation of the air-saturated acetonitrile solution of $Ph_2I^+PF_6^-$ in the presence of thiophene (2 mM).

dominated by second-order kinetics (Figure 8, blue), which is probably caused by recombination analogue to eq 9. At 15% laser power (Figure 8, red) (less bithiophene cation radicals) the decay kinetic is of mixed second order/first order nature and follows reasonably well the tail of the decay at 100% laser power.

Because the direct formation of thiophene cation radicals in the reaction with $PhI^{\bullet+}$ could not be observed by absorption in laser flash photolysis measurements, experiments were performed in an attempt to determine the thiophene cation radical by EPR. Photolysis of the ioidonium salt in the presence of thiophene in air-saturated acetonitrile solutions at room temperature generated an EPR spectrum assigned to the thiophene radical cation (Figure 9). The coupling constants (a_H) extracted from spectral simulation were found to be 3.6 and 21 G. Although these values were higher than the reported values (3.2 and 11.8 G)[20] (2.5 and 13 G),[21] the observed coupling pattern (Figure 9) matches the expected shape for thiophene cation radicals. In addition, the published values were measured under different conditions (radiolysis in Teflon matrix at low temperature). The coupling constants of polar radicals are known to be affected by the polarity of the medium. In the previously published studies a nonpolar Teflon matrix was used, whereas in our experiments the polar acetonitrile was used as solvent.

Product analysis of the solution at the early stages of the photolysis did not give conclusive results as it contained a mixture of many different oligomers (dimers, trimers, tetramers, and higher oligomers) as well as the iodonium salt and its various decomposition products. However, prolonged irradiation caused deposition of the polythiophene on the walls of the quartz vessel.

Conclusions

Laser flash photolysis and EPR studies demonstrate that photoinduced step polymerization of thiophene by onium salts proceeds by successive electron-transfer reactions. Radical cations formed from the photolysis of onium salts rapidly oxidize thiophene to the radical cation, leading to the formation of dimers through proton release and coupling reactions. Repeated similar reactions of dimers and other oligomers eventually yield polythiophene.

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