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A Photochemical Study of Poly(3-hexylthiophene)

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ABSTRACT: Poly(3-hexylthiophene) undergoes chain scission in organic solvents when irradiated with UV-vis light. Quantum yields of chain scission are dependent on the presence or absence of oxygen, the nature of the solvent, and the wavelength of incident light. Concurrent with photo chain scission is a photochemical 1,4 Diels-Alder addition of photosensitized singlet oxygen. The formation of photochemical residues in the main chain reduces the number of π-electron-conjugated sequences and leads to quenching of the excited singlet state.

Introduction

Poly(3-alkylthiophenes) are π-electron-conjugated polymers that exhibit high electrical conductivity in the oxidized state[1] and fast third-order nonlinear optical activity in the neutral state.[2] The presence of the alkyl side chain both enhances solubility in common organic solvents and decreases the glass transition temperature. As a result, they are processable, and their integration into commercial optical and electronic devices can be realized. In addition, increased solubility of poly(3-alkylthiophenes), compared to unsubstituted polythiophenes, aids characterization, and solution studies have revealed an intricate relationship between π-conjugation and polymer conformation.[3]

Since many of their technological applications are optical in nature, it is surprising that the photochemistry of polythiophenes is not well documented, although, there are numerous reports on photophysical properties.[4] It is of interest, therefore, to investigate chemical reactions that result from the interaction with UV and visible light with conjugated polyheterocycles. This paper describes a photochemical study of poly(3-hexylthiophene) (P3HT) in organic solvents.

Experimental Section

Chloroform and dichloromethane were distilled over P_2O_5. Tetrahydrofuran (Baxter, HPLC grade) was distilled over sodium. All other reagents were used as received.

Synthesis of Poly(3-hexylthiophene). 3-Hexylthiophene was synthesized by coupling the Grignard reagent of 3-bromothiophene (Aldrich) with 1-bromohexane using bis(1,3-diphenylphosphino)propane nickel(II) chloride as catalyst.[5] The product was purified by fractional distillation under reduced pressure. Polymerization of the monomer was achieved by mixing a 0.1 M solution of 3-hexylthiophene in chloroform with a 0.4 M chloroform solution of anhydrous ferric chloride.[6] The mixture was stirred for 2 h prior to precipitation into acidified methanol. The solid product was filtered and washed with NH_4OH, water, and methanol. The crude polymer was dissolved in hot dichloromethane, and insoluble products were removed by filtration. Low molecular weight products were removed by cooling the filtrate and adding methanol. The precipitate was filtered and dried in a vacuum oven. The polymer possessed IR bands at 3027, 2930, 2859, 1458, 819, and 725 cm^{-1}.

Instrumentation. Infrared spectra were recorded on a Bomem Michelson FTIR (120 Series). UV-vis absorption spectra were recorded on a Perkin-Elmer Lamda 3A UV-vis spectrophotometer at 25 °C. Solutions for UV-vis analysis were 5×10^{-6} g/mL in concentration, and the optical path length was 1 cm. Front-face fluorescence measurements were performed on a LS100 spectrofluorometer (Photon Technology International Inc.) using solutions 1×10^{-4} g/mL in concentration.

Determination of Molecular Weight. Molecular weight distribution curves of polymers were determined by gel permeation chromatography (GPC) using 10^5-, 10^4-, and 10^3-Å μ-Styragel columns at 25 °C. Polymers were eluted with tetrahydrofuran and detected using a UV-vis spectophotometer (Spectra-Physics, Model SP8000) and a refractive index detector (Waters, Model R400). Data were acquired, stored, and analyzed by using an IBM personal computer and custom-written software.

Polystyrene standards (Polymer Labs, Inc.) of molecular weights ranging from 233 000 to 750 were used for calibrating GPC columns for hydrodynamic volume versus elution volume. The polystyrene calibration curve was converted to a P3HT-based calibration using eq 1 where M_{P3HT} and M_{PS} are the molecular weights of P3HT and polystyrene, respectively, and K_{P3HT}, a_{P3HT}, K_{PS}, and a_{PS} are the corresponding Mark-Houwink constants.

$$\log M_{P3HT} = \frac{1}{1 + a_{P3HT}} \log \frac{K_{PS}}{K_{P3HT}} + \frac{1 + a_{PS}}{1 + a_{P3HT}} \log M_{PS} \quad (1)$$

K and a values for polystyrene and P3HT were taken as 1.29×10^{-2} cm^3/g and 0.713 and 2.28×10^{-3} cm^3/g and 0.96, respectively.[7,8]

Photolyses. Solutions of polymers (4 mL, 0.1 mg/mL) were irradiated in 1-cm quartz cuvettes. Solutions were either O_2-saturated with medical air or oxygen or deoxygenated by purging with oxygen-free nitrogen. The temperature of the cell was kept constant at 25 °C by a cooling block and a circulating water bath. The illumination source was a 150-W mercury lamp (Illumination Industries Ltd.). The wavelength of irradiation was selected by using an appropriate 10-nm-band-width interference filter. The intensity of light striking the cell was determined by ferrioxalate actinometry. All the light entering the cuvette was absorbed. The photonic flux was 1.91×10^{-6}, 4.22×10^{-6}, and 5.91×10^{-6} einstein/min at 313, 366, and 436 nm, respectively, unless otherwise stated. Samples of 50 μL were extracted periodically for analysis by GPC and UV-vis spectrophotometry. Fluorescence measurements were performed on the total volume of irradiated solution.

Photo chain scission of P3HT was followed by GPC. The number of main-chain breaks was calculated by using

$$S = (w/M_n)[(M_{n0}/M_n) - 1]I_{abs} \quad (2)$$

where S is the average number of chain breaks per polymer chain, w is the mass of polymer irradiated (g), M_{n0} and M_n are the initial and final number-average molecular weights of the polymer, and I_{abs} is the number of einsteins absorbed. The quantum yield for chain scission was obtained from the gradient of a plot of number of chain breaks against irradiation dose.

Results

UV-Vis and Fluorescence Spectroscopy.

UV-vis absorption spectra of P3HT were recorded in tetrahydrofuran, chloroform, benzene, toluene, and dichloromethane. A broad absorption at 430 nm is evidence of

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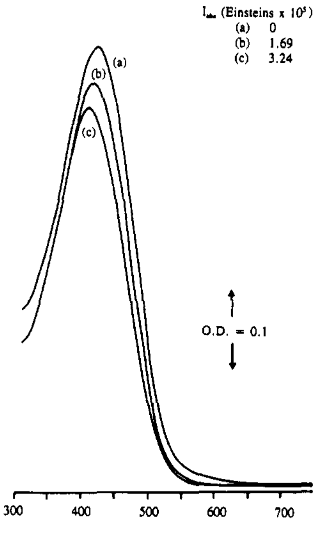


Figure 1. UV-vis spectra of P3HT during irradiation with 313-nm incident light. Concentration of photolyzed solution = 1 × 10^{-4} g/mL in O_2-saturated chloroform. Solution diluted to 5 × 10^{-6} g/mL for UV-vis spectra.

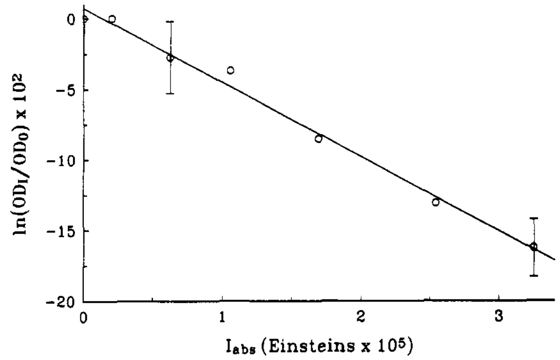


Figure 2. Plot of ln (OD_I/OD_0) against irradiation dose. OD_0 and OD_I represent optical densities (at λ_{max}) before and after irradiation. Data taken from Figure 1.

Table I
Effect of Irradiation Dose on λ_{max} of Poly(3-hexylthiophene)[a]

I_{abs}, ×10^5 einstein	λ_{max}, nm	I_{abs}, ×10^5 einstein	λ_{max}, nm
0.00	430	1.09	424
0.21	429	2.55	421
0.62	428	3.25	416
1.06	426		

[a] Irradiation wavelength = 313 nm; O_2-saturated $CHCl_3$; solution volume = 3.6 mL; 0.1 mg/mL of P3HT.

extensive π-electron delocalization. From the similarity of the individual absorption spectra delocalization is inferred to extend over a similar number of thienyl residues in each of these solvents.

Irradiation of P3HT in O_2-saturated solutions causes a decrease in the optical density (Figure 1). This decrease is linear with irradiation time and indicates a reduction in the number of π-electron-conjugated sequences with irradiation. Figure 2 shows a logarithm plot of the ratio of change in optical density versus irradiation dose. A slight shift in the absorbance maxima is also observed (Table I), which is interpreted as indicating a decrease in the average π-conjugation length.

Solutions of P3HT fluoresce strongly when irradiated with light of wavelengths less than 550 nm. The broad emission, centered at approximately 580 nm, has a lifetime of ~600 ps.[4g] Fluorescence is partially quenched by the presence of oxygen, as shown in Figure 3. Integration and comparison of the fluorescence intensities show that the ratio of fluorescence quantum yields in the presence and absence of dissolved oxygen is in agreement with Stern-Volmer quenching theory.[9]

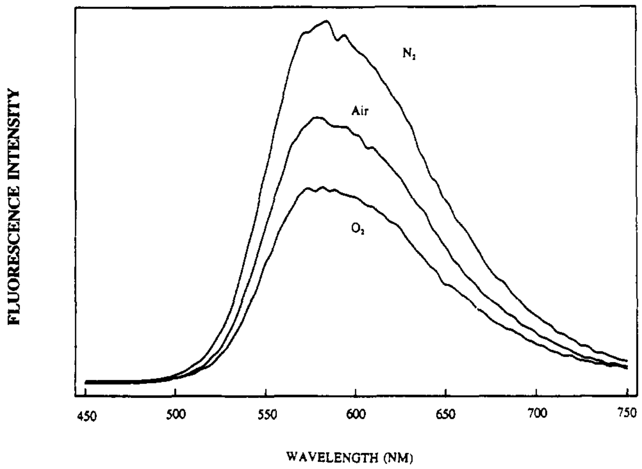


Figure 3. Fluorescence spectra of P3HT in $CHCl_3$ purged with N_2, air, and O_2. Excitation wavelength = 400 nm. Concentration of P3HT = 1 × 10^{-4} g/mL.

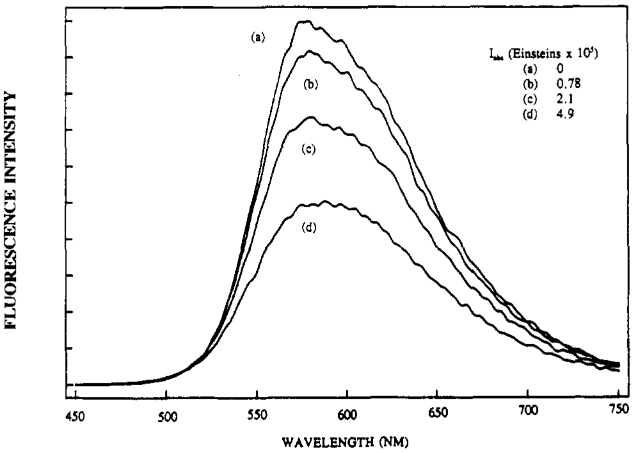


Figure 4. Fluorescence spectra of P3HT during irradiation at 313 nm. [P3HT] = 1 × 10^{-4} g/mL in O_2-saturated chloroform. Excitation wavelength = 400 nm.

The intensity of fluorescence from P3HT is permanently reduced by irradiation in O_2-saturated solutions as shown in Figure 4. Plots of log $(I_I/I_{I=0})$ against irradiation dose are linear, indicating a pseudo-first-order reaction rate (Figure 5).[10] From the gradient, the rate of decrease in fluorescence intensity is 4.47 min^{-1}, which is 2.1 times greater than the rate of decrease in optical density. It is assumed that the decrease in the optical density represents a reduction in the number of π-electron-conjugated sequences. Thus, the decrease in fluoresence intensity, which is twice as fast, cannot solely be explained in terms of a photochemical event that disrupts conjugation (see the Discussion section).

Photo Chain Scission. Irradiation of P3HT in O_2-saturated organic solvents results in a decrease in the molecular weight of the polymer, as is evident from the gel permeation chromatograms shown in Figure 6. The rate of chain scission is markedly affected by the presence of oxygen (Figure 7) and by the wavelength of the irradiating light. Figure 8 shows the kinetics of photolysis of O_2-saturated solutions of P3HT in $CHCl_3$ using different wavelengths of incident light. Quantum yields of chain scission decrease in the order 313 > 366 > 436 nm.

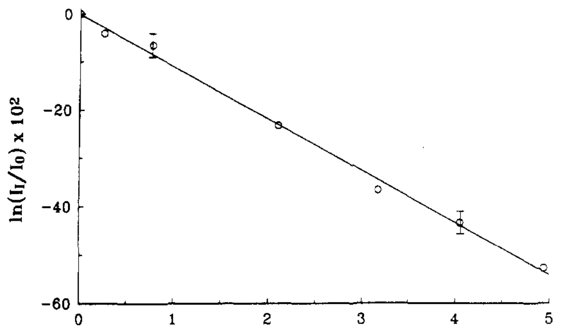


Figure 5. Plot of ln (I_l/I_0) against irradiation dose. I_0 and I_l represent integrated fluorescence intensities of P3HT in O_2-saturated $CHCl_3$ before and after irradiation. Data taken from Figure 4.

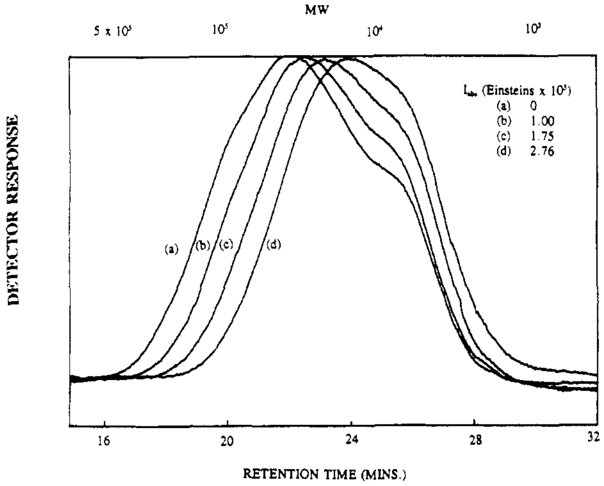


Figure 6. Gel permeation chromatograms of P3HT during irradiation with 313-nm incident light in O_2-saturated $CHCl_3$. Eluant is THF.

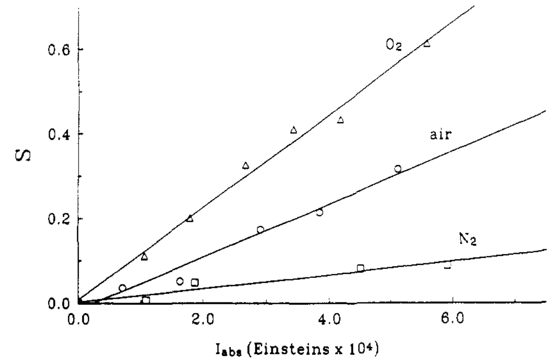


Figure 7. Effect of oxygen on the photoscission of P3HT in $CHCl_3$. Incident wavelength = 313 nm. S = number of chain breaks per polymer chain. M_{n0} = 9300.

Quantum yields are summarized in Table II.

The solution photochemistry of many polymers is often dependent on the nature of the solvent. In the present study the nature of the solvent had a pronounced effect on the rate of photo chain scission. Quantum yields of chain scission in O_2-saturated tetrahydrofuran were 22, 12, and 14 times smaller at 313, 366, and 436 nm, respectively, compared to values obtained in $CHCl_3$. In O_2-saturated benzene, quantum yields were even lower (Table II).

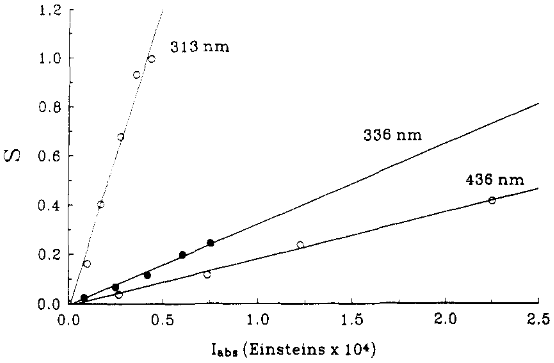


Figure 8. Effect of wavelength of incident light on the photoscission of P3HT in O_2-saturated $CHCl_3$. S = number of chain breaks per polymer chain. M_{n0} = 9300.

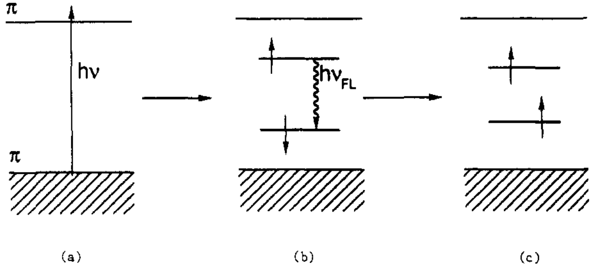


Figure 9. Evolution of the photoexcited π-system showing the π-π* transition (a), formation of the excited singlet state (neutral bipolaron) (b), and the triplet configuration (c). Fluorescence is indicated by $h\nu_{FI}$.

Table II
Quantum Yields of Photo Chain Scission of Poly(3-hexylthiophene)[a]

wavelength of incident light, nm	solvent	purging gas	$\Phi_S \times 10^5$
313	$CHCl_3$	O_2	82.1 ± 2.0
313	$CHCl_3$	N_2	8.3 ± 1.8
366	$CHCl_3$	O_2	11.9 ± 0.4
436	$CHCl_3$	O_2	6.9 ± 0.5
313	THF	O_2	4.0 ± 0.8
313	THF	air	2.2 ± 0.4
313	THF	N_2	0.57 ± 0.04
366	THF	O_2	0.49 ± 0.01
436	THF	O_2	0.47 ± 0.04
313	benzene	O_2	3.6 ± 0.4

[a] At 25 °C.

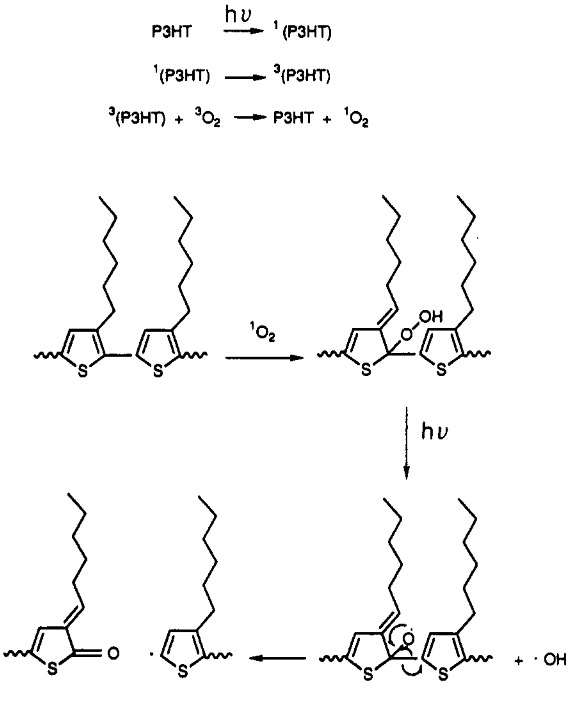
Discussion

The lowest triplet state of oligomeric thiophenes is known to be an efficient singlet oxygen photosensitizer.[11] Bimolecular reaction rate constants for the interaction of thiophene triplets with oxygen in ethanol are reported by Reyftmann et al. to be 4 × 10^{-9} and 1.5 × 10^{-9} $M^{-1}\,s^{-1}$ for α-terthienyl (α-T) and α-quaterthienyl (α-Q), respectively.[11b] Triplet lifetimes of α-T and α-Q in O_2-free ethanol are 57 and 45 μs, respectively.

It is reasonable to extrapolate these studies and propose that longer chain thienyl molecules (i.e., P3HT) also form excited triplet states, which photosensitize the formation of singlet oxygen. However, a direct analogy with small-molecule thiophenes should be approached with caution since electronic excitation of π-conjugated heterocycles results in the formation of electron-hole pairs, polarons, and bipolarons rather than discrete excited singlet and triplet states. A mechanism for excitation and triplet formation in polythiophenes is shown in Figure 9.

In this scheme, excitation promotes a π-band electron into the π*-band to form an excited electron-hole pair. The latter relaxes rapidly to yield an excited, localized singlet state in the form of a neutral bipolaron. Fluorescence is due to a radiative transition from the upper to lower energy subgap and should exhibit a large Stokes

Scheme I



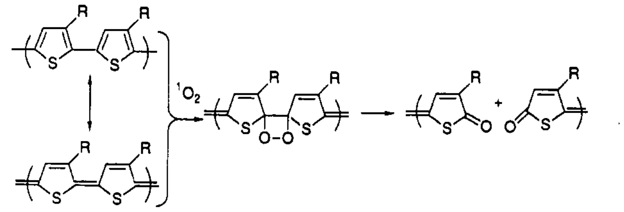
shift. The Stokes shift for P3HT is 125 nm. This is much larger than α-terthiophene (59 nm) and α-quaterthiophene (64 nm), in agreement with the formation of electronic subgaps. If, on the other hand, the electron spins of the neutral bipolaron become parallel, a longer lived triplet state is obtained. It is postulated that the latter configuration is responsible for photosensitization of singlet oxygen, in analogy with oligomeric thiophenes.

It is well established that singlet oxygen undergoes addition to polymers that possess double bonds. The product is an allylic hydroperoxide, which, upon photolysis, initiates an autocatalytic chain reaction leading to chain scission.[12] It is postulated that photo chain scission of poly(3-hexylthiophene) occurs via the hydroperoxide route since the number of double bonds in the polymer is large, and thiophenes are efficient singlet oxygen photosensitizers. This is supported experimentally by the marked dependence of quantum yield for chain scission on (1) the wavelength of incident light, (2) the nature of the solvent; and (3) the presence of dissolved oxygen.

A proposed mechanism for chain scission in P3HT is shown in Scheme I. Absorption of a photon and intersystem crossing results in the formation of an excited triplet state, which subsequently sensitizes the formation of singlet oxygen. Singlet oxygen can attack the thienyl ring bonds at four positions. However, the predominant mechanism must involve singlet oxygen addition at the 2-position of a 3-hexylthienyl unit in order to form a hydroperoxide, which upon photolysis leads to chain scission. Photolysis of the O–O bond yields the corresponding alkoxy and hydroxyl radicals. Chain scission then proceeds as a result of β-cleavage of the polymeric alkoxy radical. Formation of polythienylalkoxy radicals, by photolysis of polythienyl hydroperoxides, is thermodynamically plausible since the polymer absorbs at wavelengths that have sufficient energy to break the relatively weak O–O bond (175 kJ/mol).[13]

Ng and Guillet have measured quantum yields of decomposition for several polymeric hydroperoxides.[14] High quantum yields are observed (3–30) as a result of radical-induced chain reactions. Hydroxyl radicals and solvent radicals have been postulated as being active species that promote the chain reaction. The former is a decomposition product of hydroperoxide, while the latter are the product of radical abstraction reactions between alkoxy radicals and solvent molecules. Clearly, if chain scission occurs by the aforementioned mechanism, solvents from which atoms can be abstracted more readily will yield larger rates. Experimentally observed quantum yields of chain scission for P3HT are in full agreement with this hypothesis: $CHCl_3$, from which hydrogen atoms are easily abstracted, leads to rates of chain scission that are greater than those determined in THF. The rate of chain scission is even lower in benzene, which is well-known for its resistance to H-atom abstraction. Differing rates cannot be attributed to differing solubilities of oxygen in various solvents since the solubilities of oxygen in $CHCl_3$ and in benzene are comparable and the solubility of oxygen in THF is larger than that in $CHCl_3$.

Scheme II



Quantum yields of chain scission exhibit a strong dependency on the irradiating wavelength. Since the relative optical densities of P3HT at the incident wavelengths 313, 366, and 436 nm are 1.0, 2.1, and 4.1, respectively, the variation in quantum yield is most likely due to optical filtering by the polymer, which reduces the rate of photolysis of the polythienyl hydroperoxide intermediate.

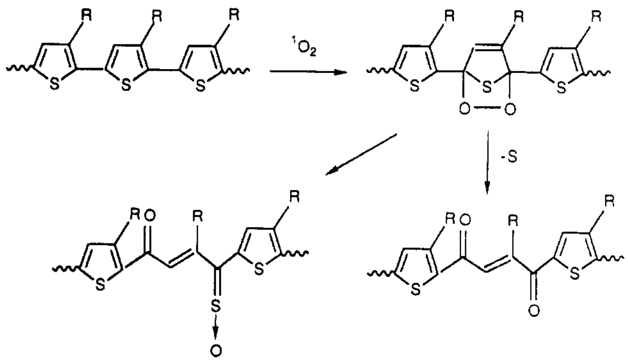
An alternative mechanism involving singlet oxygen (Scheme II) might conceivably contribute to photochemical chain scission, namely, formation of a dioxetane followed by cycloreversion. However, the dependence of quantum yields on the nature of the solvent, and on the wavelength of the incident light cannot be explained by this mechanism, thus precluding it as being a dominant pathway.

The rate of decrease in the optical density of the P3HT solutions during photolysis provides information on the rate of decrease of π-electron-conjugated sequences. Quantum yields for this process can be expressed by eq 3. where [CS] represents the average concentration of

$$\Phi = \frac{\text{rate of decrease of optical absorbance}}{\text{rate of photons absorbed}} = \frac{k_{cs}[\mathrm{CS}]}{I_0} \qquad (3)$$

π-conjugated sequences and k_{cs} is the pseudo-first-order rate constant for the decrease in the number of π-conjugated sequences. k_{cs} was 2.16 min^{-1} when the number of einsteins absorbed per minute was 4.14×10^{-7}, from which $\Phi = 5200[\mathrm{CS}]$ is obtained. Although it is not possible to accurately determine [CS], upper and lower limits can be estimated: Themans et al. have calculated theoretical bandgaps of thiophene oligomers and polymers for a series of different π-conjugation sequence lengths.[15] By comparison of experimental and theoretical absorption data for the P3HT samples used in this study, it is estimated that the π-conjugation length is comprised of at least 10 repeating units. Since irradiated solutions were 5.9×10^{-4} M in concentration, based on the repeating 3-hexylthiophene monomer unit, the upper limit for [CS] is $\sim 5.9 \times 10^{-5}$ M. A lower limit for [CS] was estimated, assuming the largest possible conjugation sequence length is equiv-

Scheme III



alent to the average degree of polymerization, $\overline{DP}$. $\overline{DP}$ was determined by molecular weight analysis to be 56, and, thus, the lower limit for [CS] was 1.05×10^{-6} M. When the limits for [CS] are used, the upper and lower limits for the quantum yield of the loss of conjugated sequences are 0.30 and 0.05. Both these values are significantly larger than the quantum yields of chain scission.

It is evident that a photochemical process responsible for the decrease in optical density is not solely photo chain scission since the quantum yields of the latter are relative low. Skold and Schlessinger and Wasserman and Strehlow have reported that singlet oxygen undergoes a 1,4 Diels–Alder addition with thiophenes, the intermediate of which rearranges to yield a sulfine and a *trans*-diketone.[16] Both of these products exhibit strong, and characteristic, IR absorption bands. FTIR studies of P3HT solutions after extensive photolysis show several new IR absorptions: 1647 cm^{-1} (C═O); 1420 cm^{-1} (C═C); 1209 and 1161 cm^{-1} (C═S→O).[17] These are consistent with a Diels–Alder addition of singlet oxygen to thienyl residues. The mechanism illustrated in Scheme III was adapted from analogous reactions with small-molecule thiophenes.[16a] However, it should be noted that a plausible mechanism of chain scission via Diels–Alder addition of singlet oxygen cannot be deduced since neither the sulfine or diketone can cleave upon photolysis. Chain scission by a Norrish type I cleavage of the C—(C═C) bond requires ~335 kJ/mol of energy, but the highest energy singlet state is only 239 kJ/mol (estimated from the shortest fluorescence wavelength, ~500 nm). Scission by a Norrish type II mechanism is precluded since neither the sulfine nor the diketone possess abstractable β- or γ-hydrogens in the main chain.

The pseudo-first-order rate constant for the decrease in fluorescence is 4.47 min^{-1}, which is approximately twice as large as the rate of decrease in the optical density. This indicates that the decrease in fluorescence is not solely the result of a decrease in the number of π-conjugated sequences. Intramolecular quenching of the excited singlet state by sulfine or diketone residues is the most likely reason for the more rapid decrease in the fluorescence compared to the optical density.

Conclusion

Poly(3-hexylthiophene) undergoes chain scission when irradiated with UV–vis light. The quantum yields of chain scission are greatly enhanced by the presence of oxygen and solvents that promote free-radical reactions. Although quantum yields are low, overall rates of chain scission with solar irradiation might be high due to the broad absorption band in the visible region of the spectrum. Photo chain scission is accompanied by a decrease in the number of π-conjugated units and an increase in the quenching of the excitation. The quantum yields of the latter two processes are significantly greater than those of photoscission.

Disruption of the π-system will lead to a diminished state of conjugation and consequently, a reduction in electronic conductivity and nonlinear optical activity. The interactions and effects of UV–vis irradiation on the electrooptical properties of solid, amorphous films of poly(3-alkylthiophenes) are currently under investigation.

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(10) $I_{t=0}$ and I_t are the integrated fluorescence intensities before and after irradiation.

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Registry No. P3HT, 104934-50-1; O_2, 7782-44-7.