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Communications to the Editor

Photochain Scission of the Soluble Electronically Conducting Polymer: Poly(3-hexylthiophene)

Introduction. Poly(3-alkylthiophenes) are of considerable interest due to their high electrical conductivity in the oxidized state[1] and fast third-order nonlinear optical properties in the neutral state.[2] In addition, they are melt processable and exhibit high solubility in organic solvents. They are, therefore, exceptional materials for incorporation into electronic or electrooptical devices.

Although considerable attention has been paid to the electronic and optical properties of polythiophenes,[3] little is known of their photochemistry. In view of their potential applications, many of them involving their interaction with electromagnetic radiation, it is pertinent to investigate photochemically induced reactions of poly(3-alkylthiophenes). This paper describes preliminary results of photochain scission of poly(3-hexylthiophene) (P3HT) in organic solvents.

Experimental Section. Chloroform and dichloromethane were distilled over P_2O_5. Tetrahydrofuran (Baxter, HPLC/UV grade) and all other reagents were used as received.

Poly(3-hexylthiophene) was synthesized by the method described by Sugimoto et al.[4] 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 by using a UV/vis spectrophotometer (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 Laboratories, Inc.) of molecular weights ranging from 233 000 to 750 were used for calibrating the columns for hydrodynamic volume versus elution volume. The polystyrene calibration curve was converted to a P3HT-based calibration curve by using eq 1 where M_{P3HT} and M_{PS} are the molecular weights of

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

P3HT and polystyrene, respectively, and K_{P3HT}, a_{P3HT}, K_{PS}, and a_{PS} are the corresponding Mark–Houwink constants. 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.[5,6]

Solutions of polymers (4 mL, 0.1 mg/mL) were irradiated at 25 °C by using a 150-W mercury lamp (Illumination Industries, Ltd.) and appropriate 10-nm-bandwidth interference filters. 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. Samples (50 μL) were extracted periodically for analysis by GPC.

The number of main-chain breaks was calculated by using

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

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 is obtained from the gradient of a plot of the number of chain breaks against irradiation dose.

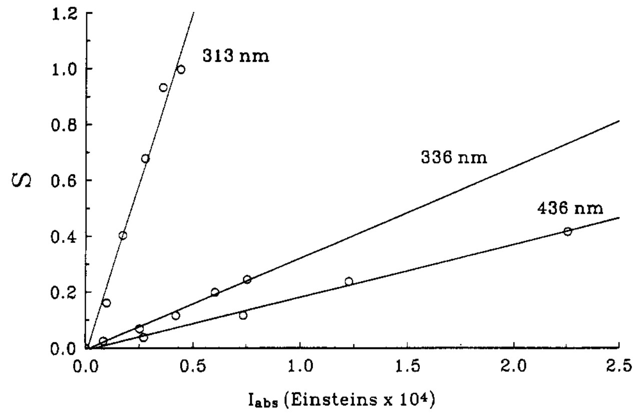

Figure 1. Effect of oxygen on the photochain scission of P3HT in THF at 313 nm. M_{n0} = 9300.

Table I
Quantum Yields of Photochain 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.

Results. Irradiation of P3HT in O_2-saturated organic solvents, using 313-nm light, decreases the molecular weight of the polymer. The rate of chain scission is greatly reduced when oxygen is absent, as illustrated by Figure 1. The quantum yields of chain scission are shown in Table I.

The rate of chain scission is strongly dependent on the wavelength of the irradiating light. Figure 2 shows the kinetics of photolysis of O_2-saturated solutions of P3HT in $CHCl_3$ using light of wavelength 313, 366, and 436 nm. The quantum yields decrease in the order 313 > 366 > 436 nm. The respective quantum yields of chain scission are also listed in Table I.

The nature of the solvent has a pronounced effect on the rate of photoinduced chain scission. In O_2-saturated tetrahydrofuran the quantum yields of chain scission decreased, compared to $CHCl_3$, by factors of 22, 12, and 14 at 313, 366, and 436 nm, respectively. In N_2-purged THF the quantum yield was 14 times smaller than that observed in deoxygenated $CHCl_3$ at 313 nm. In O_2-saturated benzene, the quantum yield was 3.64×10^{-5} at

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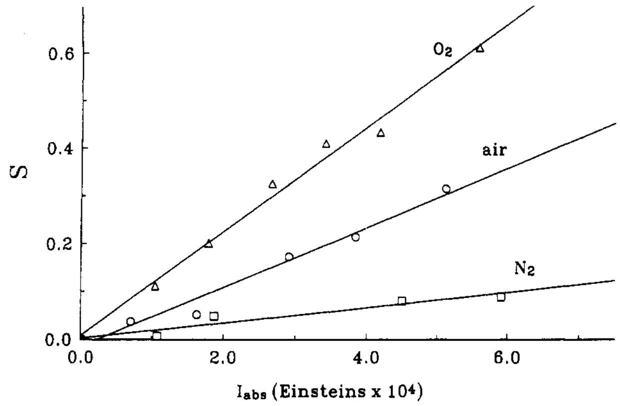


Figure 2. Effect of wavelength of irradiation on the photochain scission of P3HT in $CHCl_3$. M_{n0} = 9300.

313 nm, slightly lower than that determined in THF at 313 nm. These results are tabulated in Table I.

Discussion. The purpose of this paper is to provide qualitative and quantitative evidence for photochemically induced chain scission in this important class of materials. A detailed study of the mechanism of photochain scission is currently under way. Evidently, the lowest triplet state of oligomeric thiophenes is an efficient singlet oxygen photosensitizer.[7] Furthermore, singlet oxygen undergoes a 1,4 Diels–Alder addition reaction with thiophenes, the intermediate of which rearranges to yield a sulfine.[8] The latter can be detected by IR since this functional group exhibits strong, and characteristic, absorption bands. Following photolysis of P3HT in the presence of oxygen, the residual polymer absorbs strongly at 1209 and 1161 cm^{-1}, indicating the formation of a sulfine residue. This is indirect evidence for the photosensitization of singlet oxygen by poly(3-hexylthiophene).

However, a plausible mechanism of chain scission cannot be deduced either from the Diels–Alder addition of singlet oxygen to P3HT or from the products of this reaction. Thus an alternative mechanism must be prevalent: It is well established that singlet oxygen undergoes addition to polymeric double bonds to yield an allylic hydroperoxide and that photolysis of the hydroperoxide initiates an autocatalytic chain reaction which leads to chain scission.[9] It is inferred that the hydroperoxide mechanism is responsible for photochain scission of P3HT since a large number of polymeric double bonds exist, singlet oxygen is produced in situ, and quantum yields for chain scission are low and are markedly dependent on the nature of the solvent and on the incident wavelength. Furthermore, FTIR studies of P3HT after prolonged photolysis reveal IR bands that are consistent with the presence of a thienyl ketone and an olefin (1647 and 1420 cm^{-1}).

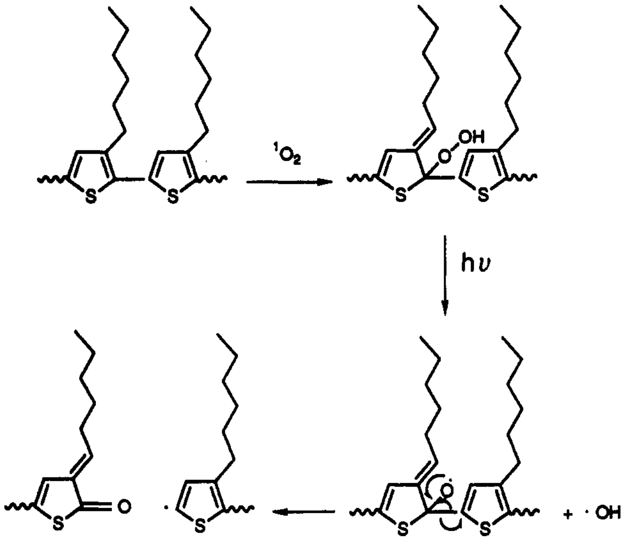
In the case of P3HT, singlet oxygen must attack the 2-position of a 3-hexylthienyl unit in order to abstract a β-hydrogen and form the hydroperoxide. Photochemical cleavage of the O–O bond yields the corresponding alkoxy radical and one hydroxy radical. Chain scission then proceeds as a result of β-cleavage of the polymeric alkoxy radical. Formation of polythienyl alkoxy 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).[10] A tentative model for the photolysis of poly(3-hexylthiophene) is given in Scheme I.

Scheme I

$$\mathrm{P3HT} \xrightarrow{h\nu} {}^{1}(\mathrm{P3HT})$$

$$^{1}(\mathrm{P3HT}) \longrightarrow {}^{3}(\mathrm{P3HT})$$

$$^{3}(\mathrm{P3HT}) + {}^{3}O_2 \longrightarrow \mathrm{P3HT} + {}^{1}O_2$$



Quantum yields of decomposition of polymeric hydroperoxides can exceed unity as a result of radical-induced chain reactions. The active chain reaction carrying species have been postulated by Ng and Guillet as hydroxy and solvent radicals.[11] The latter are produced by radical abstraction reactions between alkoxy radicals and solvent molecules. Clearly, the nature of the solvent plays a large role on the rate of chain scission: solvents from which atoms are abstracted more readily yield larger rates. This hypothesis is in agreement with the experimentally observed quantum yields of chain scission. $CHCl_3$, from which chlorine atoms are easily abstracted, leads to faster rates of chain scission than THF or benzene. Alternatively, differing rates might result from differing solubilities of oxygen in the various solvents. However, this is rejected since the solubilities of oxygen in $CHCl_3$ and in benzene are comparable (±10%) and the solubility of O_2 in THF is considerably larger than that in $CHCl_3$. The quantum yields clearly do not reflect the differences in concentration of dissolved oxygen.

The relative optical densities of P3HT are 1, 2.09, and 4.09 at 313, 366, and 436 nm, respectively. The strong dependency of wavelength on the quantum yield may, therefore, be due to an optical filtering effect by P3HT, which subsequently reduces the rate of photolysis of hydroperoxides. Studies are currently under way to confirm this mechanism and to determine the generality of photochain scission in polyheterocycles.

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Steven Holdcroft

Department of Chemistry and Biochemistry
Simon Fraser University
Burnaby, British Columbia, Canada V5A 1S6

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