Mechanisms of Photodegradation of Poly(3-alkylthiophenes) in Solution

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ABSTRACT: Poly(3-hexylthiophene) degrades in nonaqueous solvents containing dissolved molecular oxygen when irradiated with UV or visible light. Degradation takes the form of both reduced π-conjugation and chain scission. The former manifests itself as photobleaching and is largely the product of photosensitization and reaction of singlet oxygen. Chain scission occurs via the classical route of photooxidation where scission is initiated by photolysis of trace amounts of transition-metal salts. In the case of poly(3-hexylthiophene), prepared by chemical oxidation using $FeCl_3$, the photoactive impurities are iron(III) salts. Free-radical attack on thienyl rings provides an additional, but minor, route to photobleaching. Similar polymers prepared electrochemically and by Grignard polycondensation reactions also undergo photochain scission but to a lesser degree than polymers prepared by $FeCl_3$. The variation in rates of scission is attributed to differences in the nature and concentration of the impurities.

Introduction

Unique microelectronic,[1-6] optical,[7,8] and photonic applications,[9-13] are emerging in which π-conjugated polymers and oligomers complement, or even, replace conventional inorganic and metallic components. As a result these materials are under intense chemical, physicochemical, and electronic scrutiny. Many are intractable and therefore difficult to use. For this reason poly(3-alkylthiophenes) (P3AT) are attracting considerable attention since they can be easily handled yet exhibit the interesting electronic and optoelectronic properties of π-conjugated polymers. This report primarily focuses on this class of polymers.

Many interesting characteristics of poly(3-alkylthiophenes), and π-conjugated polymer in general, result from their interaction with, and response to, light. The materials absorb in the visible region of the electromagnetic spectrum and exhibit subnanosecond luminescence. In solution, intersystem crossing from the singlet excited state is efficient, leading to triplets from which radical cations are produced in the presence of an electron acceptor.[14,15] In solid films, where neighboring chains may act as an electron acceptor, radical cations can give rise to polarons and bipolarons.[16-19] From a photochemical point of view, formation of a longer lived triplet may provide a route to photochemical reaction and photochemical degradation, yet detailed reports concerning the photochemistry of π-conjugated polymers are sparse.[5,20-24] We have recently shown that poly(3-alkylthiophenes) do indeed undergo photochemical reactions including photobleaching, chain scission, and cross-linking.[20-22] Mechanisms for these phenomena have been speculated on the basis of published literature on small-molecule analogs.[5,20-22] We now present results of a detailed study which increases our understanding of the photochemical reactions of poly(3-alkylthiophenes) in solution. Primarily, we have used poly(3-hexylthiophene) (P3HT) as a model polymer since it has been fully characterized and its molecular weight can be determined with reasonably accuracy.[25]

Experimental Section

Chemicals and Instrumentation. All chemicals and solvents, including chloroform (Caledon, spectroscopic grade), THF (BDH Chemicals, HPLC grade), anthracene (Matheson Coleman & Bell), and anhydrous ferric chloride (BDH Chemicals), were used as received.

UV-vis spectra were recorded on a Perkin-Elmer Lamda 3A UV-vis spectrophotometer at 25 °C. Infrared spectra were recorded on a Bomem Michelson FTIR (120 Series). ^1H and ^{13}C NMR were obtained using 400-MHz and 100.6-MHz Bruker AMX400. Mössbauer spectroscopy was performed using a NSEC Model AM1 system. Atomic absorption measurements were carried out using a Perkin-Elmer 1100 B AA spectrophotometer.

Synthesis of Poly(3-hexylthiophene). 3-Hexylthiophene was synthesized by coupling the Grignard reagent of 1-bromohexane (Aldrich) with 3-bromothiophene using [1,3-bis(1,3-diphenylphosphino)propane]nickel(II) chloride ($Ni(dppp)_2Cl_2$) as catalyst.[26] Poly(3-hexylthiophene) (P3HT) was synthesized by three routes: (i) chemical oxidative coupling using $FeCl_3$; (ii) Grignard synthesis; (iii) electropolymerization.

(I) Oxidative Coupling. Polymerization by chemical oxidative coupling was performed according to the procedure described by Sugimoto et al.[27] The solid product was filtered and washed successively with NH_4OH (28%), water, and finally acidified 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 under reduced pressure at 50 °C. A fraction of the sample was purified further by Soxhlet extraction using methanol (2 days) and acetone (5 days). Subsequently, a fraction of this polymer was purified even further by treating a solution of the polymer in $CHCl_3$ with NH_4OH (28%). The polymer was precipitated, washed to chloride-free waste, and dried as described above. By this route three polymer samples containing various levels of iron impurities were obtained. The number-average molecular weight, M_n, was 8500 with a molecular weight distribution (MWD) of ~3. The percentage of head-to-tail diads was 80%, giving a λ_{max} in $CHCl_3$ of 435 nm.

(II) Grignard Route. 3-Hexylthiophene (7.8 g, 46 mmol) and 12.2 g (48 mmol) of I_2 (BDH Chemicals Ltd.) were added to a mixture comprised of 18 mL of chloroform, 3 mL of concentrated HNO_3, and 3 mL of H_2O.[28] The mixture was refluxed for 16 h. The product, 2,5-diiodo-3-hexylthiophene, was purified through a silica gel column using hexane (71% yield, purity >99%). ^1H NMR (400 MHz, $CDCl_3$): δ 6.89 (1H, s), 2.50 (2H, t, J = 7.2 Hz), 1.53 (2H, m), 1.4-0.8 (9H, m). Magnesium metal (0.29 g, 12 mmol) was reacted with 4.2 g (10 mmol) of 2,5-diiodo-3-hexylthiophene in ether and the polymerization initiated by $Ni(dppp)_2Cl_2$. After 24 h the reaction was quenched with $MeOH/H_2O$. The reaction mixture was poured into 5% HCl in methanol to precipitate the polymer. The polymer was purified by repeated precipitations.[29] M_n was 10 000, MWD ~4.6, and the percentage of head-to-tail

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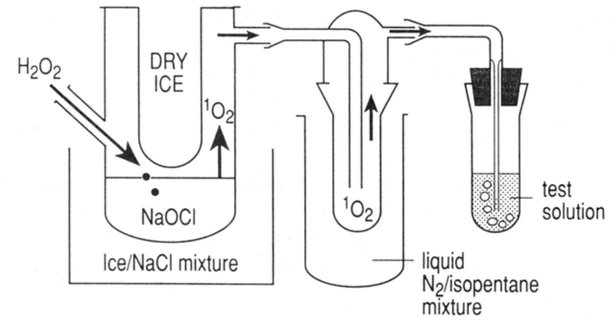


Figure 1. Experimental setup for the chemical generation of singlet oxygen.

diads was 65%, giving a λ_{max} of 415 nm in $CHCl_3$.

(III) Electropolymerization. P3HT was prepared by electrochemical polymerization of 3-hexylthiophene in acetonitrile. The polymerization vessel was a one-compartment cell equipped with an indium/tin oxide glass (ITO) anode and a platinum cathode. The polymerization was carried out at 20 °C at a constant current density of 2 mA/cm^2 under a nitrogen atmosphere. Tetrabutylammonium perchlorate was used as the electrolyte (0.2 M). The concentration of the monomer was 0.1 M. Neutral films were obtained by reversing the polarity of the electrodes after deposition. The polymer films were further reduced with NH_4OH (28%) for 24 h, washed with acidified methanol and water, and finally dried. M_n was 9000, MWD ~7, and the percentage of head-to-tail diads was 75%, giving a λ_{max} of 435 nm in $CHCl_3$.

Determination of Molecular Weight. Molecular weight distribution curves of polymers were determined by size-exclusion chromatography using 10^5-, 10^4-, and 10^4-Å μ-Styragel columns at 25 °C. Polymers were eluted with tetrahydrofuran (BDH Chemicals, HPLC grade) and detected using a UV–vis spectrophotometer (Waters Model 486) and a differential refractometer (Waters Model 410). Data were acquired, stored, and analyzed on a personal computer and custom-made software. Polystyrene standards (Polymers Labs) of molecular weights ranging from 233 000 to 750 were used for calibrating GPC columns for hydrodynamic volume versus elution volume. The polystyrene (PS) calibration curve was converted to a P3HT-based calibration using the following Mark–Houwink constants: $K_{P3HT} = 2.28 \times 10^{-3}$ cm^3/g, $a_{P3HT} = 0.96$, $K_{PS} = 1.29 \times 10^{-2}$ cm^3/g, and $a_{PS} = 0.713$.[25,30]

Photolyses. The illumination source was a 150-W mercury lamp (Illumination Industries Ltd.) focused to a 4-cm^2 beam. Irradiation was carried out using a 300-nm cut-off 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 cell was kept constant at 25 °C using a cooling block and a circulating water bath. Polymer solutions were 1 mg/mL in concentration, and the solvent was $CHCl_3$ unless otherwise stated. The optical density was ~1.0. Solutions containing 7 and 35 mg/mL in $CDCl_3$ were used for ^{1}H and ^{13}C NMR spectroscopy, respectively. For NMR measurements, irradiation was carried out under an oxygen atmosphere using a quartz cell fitted with a condenser to prevent loss of solvent and maintain a constant concentration. Samples of 1-mL volume were extracted periodically for NMR measurements. The absorption spectrum of the polymer solution was monitored with irradiation time. FTIR spectra of photolyzed polymers were recorded as thin polymer films cast onto KBr pellets. Photochain scission was determined periodically by extracting 50-μL aliquots for GPC analysis. The average number of chain scissions, S, was calculated from

$$S = (M_{n0}/M_n) - 1 \tag{1}$$

where M_{n0} and M_n are the initial and final number-average molecular weights.

Generation of Singlet Oxygen. Singlet oxygen was generated chemically using a hypochlorite/hydrogen peroxide system.[31-33] The experimental setup is depicted in Figure 1. To a cold freshly prepared solution of hypochlorite is added cold hydrogen peroxide. The rate of singlet oxygen generation was controlled by the rate of addition. The resulting gas is passed through a cold finger at −70 °C to remove water vapor and then through a trap at −150 °C to remove any traces of chlorine gas. Pure singlet oxygen was bubbled through the test solution. The generation of singlet oxygen was confirmed using anthracene as a trap. Anthracene undergoes 1,4-cycloaddition with singlet oxygen to give anthracene endoperoxide. Thermolysis yields the anthraquinone. Conversion of anthracene into anthraquinone was followed by GC. The product, anthraquinone, was identified by GCMS (m/e 208), UV (324, 273, 261 (sh), and 252 nm in $CHCl_3$), and IR spectroscopy (1675, 1595, 1355, 1320, 1305, 1285, and 690 cm^{-1}).

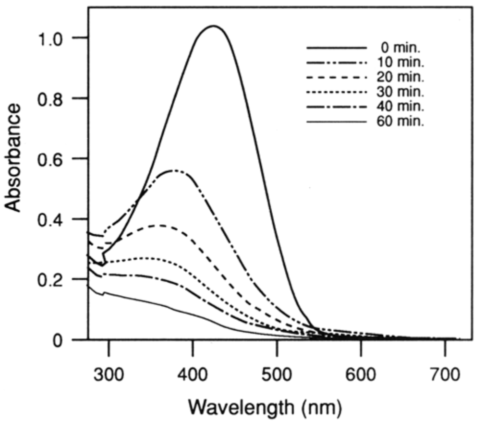


Figure 2. Change in the UV–vis absorption spectrum of poly(3-hexylthiophene) in $CHCl_3$ with time of irradiation (150-W Hg lamp, 300-nm cut-off filter).

Determination of the Iron Content in Polymer Samples. The iron content was determined by standard acid digestion procedures followed by AA detection. Dissolution of iron and breakdown of the organic materials were achieved by digesting 50 mg of polymer with 10 mL of concentrated sulfuric and nitric acids (50 vol %).[34] Stock solutions of iron were prepared by dissolving 0.250 g of iron (Baker Chemicals) in 250 mL of nitric acid (~5 mL) and distilled water. Standard iron solutions (25 mL) containing 2, 4, 8, 12, 16, and 20 ppm iron were prepared by appropriate dilution with 0.1 M HCl. A 2483-Å lamp was used.

Thermolysis of *tert*-Butyl Peroxide in the Presence of P3HT. A total of 15 mL of a benzene solution of P3HT (1 mg/mL) and *tert*-butyl peroxide was refluxed vigorously at a temperature of 160 °C under an atmosphere of oxygen for 45 h. The initiator concentration was maintained at ~0.1 M by periodic additions of the reagent. Samples of the polymer were extracted at intervals to monitor the change in optical density and the degree of chain scission.

Results and Discussion

Spectroscopic Analysis. UV–vis absorption spectra of P3HT were recorded in various solvents. Typically, a broad absorption with a maximum of ~435 nm was observed in good solvents such as $CHCl_3$, indicative of extensive π-electron delocalization.[7,35] Irradiation of the polymer in air-saturated $CHCl_3$ results in a blue shift in λ_{max} (Figure 2) and a decrease in the optical density (OD) (Figure 3). Photobleaching is attributed to disruption and shortening of the π-conjugated segments. Concurrent with photobleaching is a decrease in molecular weight of the polymer (photochain scission) (Figure 3). Number-average molecular weights of pristine polymers were 8500, representing a degree of polymerization (DP) >50. Following photolysis M_n decreased to values as low as 1400 (DP ~ 8). We will show later that photobleaching and photochain scission follow from two independent reaction pathways.

FTIR vibrational spectroscopy of polythiophenes and derivatives of polythiophene is well documented.[36-41] Data for the pristine polymer are summarized in Table I. FTIR of a P3HT solution in $CHCl_3$ (1 mg/mL) was monitored

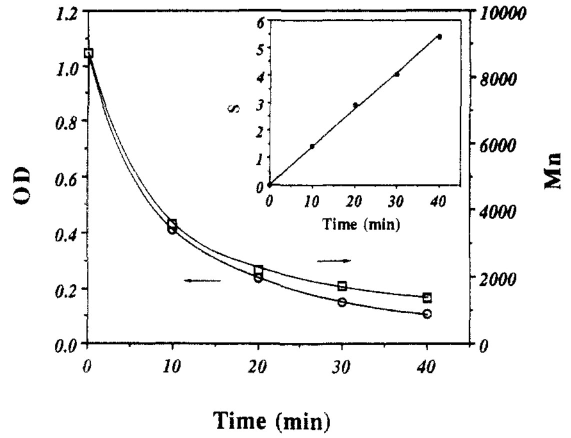


Figure 3. Decrease in the optical density of P3HT solution (λ_{max} = 435 nm) and a decrease in M_n with irradiation. Inset: number of chain scission, S, versus irradiation time.

over a period of 30 min of irradiation (Figure 4). Absorption wavenumbers and the structural assignments for new IR bands are listed in Table I. Assignments were made taking into account supporting experimental data which are presented throughout this paper. Several features concerning FTIR spectra of photolyzed samples require notation: (I) Formation of relatively strong absorption bands in the range 3700–3200 cm^{-1} which are characteristic of hydroxyl and hydroperoxy functionality. Several absorption bands indicate the presence of various alcohol species as confirmed by ^{13}C NMR. The broad absorption at 3450 cm^{-1} can be assigned to hydrogen-bonded -OH groups. The broad absorption is overlapped by a narrow band at 3580 cm^{-1} which we assign to a hydroperoxy group.[42] This assignment is supported by the symmetric and asymmetric bending of the OH group at ~1395 and 1370 cm^{-1} and in some cases by the O–O stretching vibration at ~877 cm^{-1}.[43] The presence of -OOH groups was confirmed by their partial removal and subsequent decrease of the 3580-cm^{-1} absorption band upon heating the sample *in vacuo* at 180 °C (thermal decomposition). (II) Evolution of a strong and complex band at 1800–1660 cm^{-1} characteristic of various keto and/or aldehydic groups. Formation of carboxylic acids was ruled out since treatment of the photolyzed film with methanolic KOH did not alter the spectrum and no carboxylate was observed at 1560 cm^{-1}. A weaker band at 1660 cm^{-1} is assigned to an unsymmetric olefin. These groups also have in-plane and out-of-plane bends at 1430 and 790 cm^{-1}. (III) Formation of strong bands in the region 1260–1000 cm^{-1} which indicate sulfine residues of the structure $C{=}S^+O^-$ or $C{=}S{=}O$.[44-50] The 1090- and 1020-cm^{-1} bands are attributed to a C=S stretching vibration and S–O vibrations, respectively, of $C{=}S^+O^-$. Absorptions at 1253 and 1226 cm^{-1} are characteristic vibrational modes of the alternate resonance structure, C=S=O. It will be shown that these species originate from photochemical cleavage of thienyl rings. (IV) Decrease of the aliphatic C–H stretching peak in the region 2900 cm^{-1} due to loss of the alkyl side chain. This is considered direct evidence for the participation of the alkyl chain in the photochemistry of poly(3-alkylthiophenes). (V) A decrease of the absorption bands characteristic of interannular stretching modes (1460 cm^{-1}) and disappearance of the aromatic C–H stretch and C–H out-of-plane deformation at 3055 and 823 cm^{-1}, respectively. This is attributed to disruption of the conjugated system.

^{1}H and ^{13}C NMR of P3HT in solution are also well documented,[51-53] enabling discernment in regard to changes in NMR signals upon irradiation. ^{1}H NMR spectra of pristine and photolyzed spectra are shown in Figure 5. Evolution of the resonances is summarized as follows: (I) formation of weak signals in the region 4.03 and 4.08 ppm, characteristic of olefinic protons; (II) formation of a signal at 3.75 ppm and a weak broad signal at ~7.7 ppm assigned to CH(OH) and hydroperoxy protons, respectively;[54,55] (III) evolution of a well-resolved signal at 9.8 ppm assigned to α,β-unsaturated aldehydic protons; (IV) a decrease in the aliphatic proton resonance signals, in good agreement with changes in IR spectra; (V) a decrease in the aromatic proton signal indicating ring opening or loss of aromaticity.

^{13}C NMR spectra of photolyzed polymers are in good agreement with IR and ^{1}H NMR results. Primarily, these indicate a decrease in aromatic and aliphatic signals in the regions 125–143 and 14–32 ppm, respectively; the appearance of new signals at 57 and 65 ppm assigned to primary and secondary alcohols; the formation of weak and complex signals at 120–140 ppm most likely due to olefinic signals. Carbonyl carbons in the region 220–230 ppm could not be observed due to their long relaxation time.

Photosensitizing of Singlet Oxygen by P3HT. Thiophene oligomers are known to be efficient sensitizers of the lowest excited state of molecular oxygen ($^1\Delta_gO_2$), commonly termed singlet oxygen.[15,56-59] Polythiophene and its derivatives are also candidates for being efficient singlet oxygen sensitizers.[60] This was confirmed by trapping photosensitized $^1O_2$ with anthracene as follows: An O_2-saturated $CHCl_3$ solution of P3HT containing various concentrations of anthracene ($0 \rightarrow 5 \times 10^{-4}$ M) was irradiated through a 435-nm-band-pass filter (10-nm bandwidth), ensuring that only the polymer absorbed light and the amount absorbed by anthracene was negligible. No ground-state charge-transfer complex of the two species was evident from UV–vis spectroscopy. Furthermore no mechanism of photosensitization or photoinduced electron transfer can take place between anthracene and poly(3-hexylthiophene) upon direct irradiation of the polymer.[61]

Upon irradiation of the polymer the optical absorption corresponding to the characteristic electronic and vibronic excitations of anthracene diminished. GCMS, IR, and UV–vis spectroscopic analyses confirmed the loss of anthracene and the buildup of anthraquinone (GCMS, molecular ion: m/e 208).[62] In the absence of anthracene the optical absorbance due to the π–π^* transition of the polymer decreased rapidly, while in the presence of anthracene the rate of decrease at 435 nm was suppressed (Figure 6 and Table II). No change in the rate of decrease of absorbance at this wavelength could be observed when the concentration of anthracene was $>5.0 \times 10^{-4}$ M. At this concentration of anthracene the rate of decrease in OD corresponding to the polymer was 5 times slower than when anthracene was absent. These results provide strong arguments that photosensitized $^1O_2$ is largely responsible for loss of π-conjugation and photobleaching of the polymer. The residual photobleaching of the polymer (~5%) which occurs even with large concentrations of anthracene singlet oxygen quencher is discussed later.

It was not possible to determine rates of quenching of single oxygen by the polymer or by anthracene because of the uncertainty of the concentration of singlet oxygen.[63] In addition to monitoring the decrease in OD, the corresponding change in M_n was evaluated. Table II gives the relative rates of photochain scission when the polymer is irradiated in the presence of anthracene singlet oxygen quencher. A negligible difference in the rates of chain scission is observed, indicating that chain scission is unaffected by the quenching of photosensitized $^1O_2$.

Table I. FTIR Data of P3HT[a]

wavenumber (cm^{-1})	assignment	wavenumber (cm^{-1})	assignment
(a) Pristine Polymer			
3055	C–H str (aromatic)	1377	methyl def
2955	CH_3 asym str	1260	C–C inter-ring bond str
2926	CH_2 in-phase vib	1190	wagging and twisting of methylene groups
2870	CH_3 sym str	1155	
2856	CH_2 out-of-phase vib	1090	C–H in-plane bending of thiophene ring
1655	overtone of thiophene ring	823	C–H out-of-plane def of thiophene ring
1560	$C_2{=}C_3$ and $C_4{=}C_5$ antisym and sym str modes of thiophene ring	725	rocking mode of methylene groups
1512			
1460			
(b) Photolyzed Polymer[b]			
3580	OOH str	1395	sym and asym bending of OH groups
3450	OH str	1370	
1765	CHO str	1253	C=S=O
1740		1226	
1710	C=O str (ketone)	1090	$C{=}S^+O^-$
1685		1920	
1650	C=C str	924	C–O str
1625		790	C–H def (olefin)
1431	C–H in-plane def (olefin)		

[a] Films cast on KBr disks. [b] Only new bands appearing upon photolysis are shown.

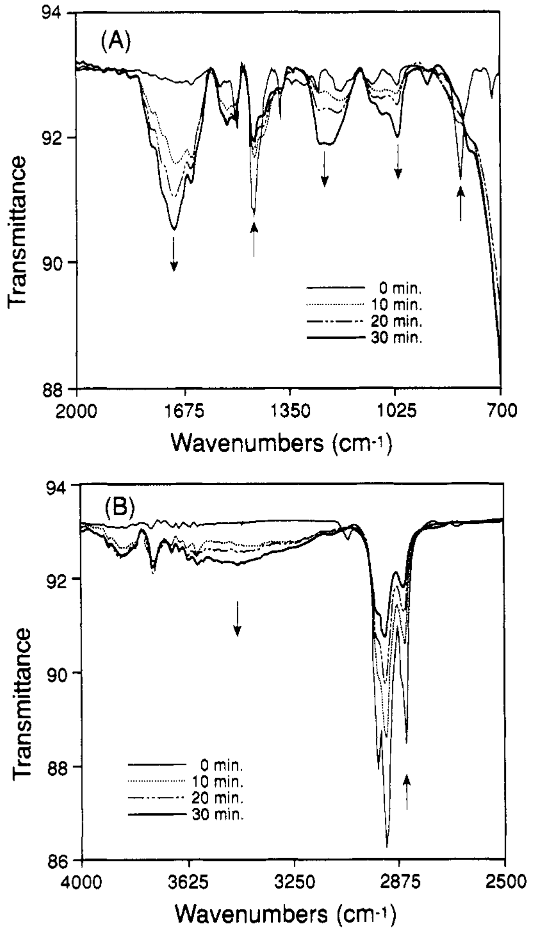


Figure 4. (A and B) FTIR of P3HT films on KBr disks as a function of time of irradiation. Photolyzed in $CHCl_3$ (1 mg/mL).

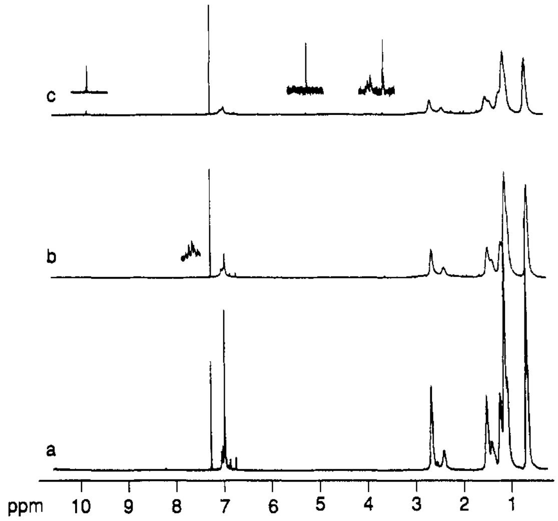


Figure 5. ^1H NMR of P3HT in $CDCl_3$ before (a) and after photolysis at (b) 4 and (c) 12 h.

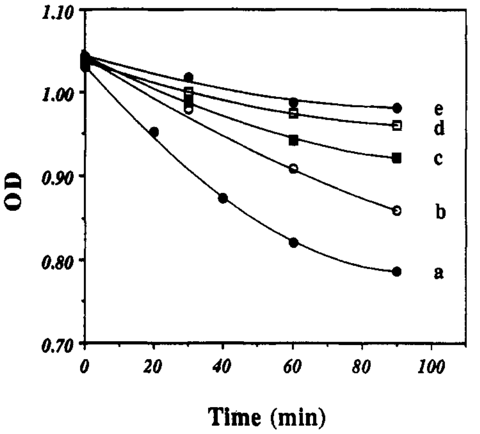


Figure 6. Decrease in the optical density of poly(3-hexylthiophene) in $CHCl_3$ (1 mg/mL; λ_{max} = 435 nm) with time of irradiation and in the presence of anthracene. [Anthracene]: (a) 0, (b) 1.25 × 10^{-4}, (c) 2.5 × 10^{-4}, (d) 3.75 × 10^{-4}, (e) 5 × 10^{-4} M. Samples were irradiated through a 435-nm-band-pass filter.

Reaction of P3HT with Chemically Generated Singlet Oxygen. The literature is rich with methodology for generation of singlet oxygen. Common systems use triphenylphosphine/ozone,[64] hypochlorite/hydrogen peroxide,[31-33] microwave discharge,[65] or photosensitization.[66,67] The hypochlorite/hydrogen peroxide system was chosen for our studies since it does not contaminate the test solution with impurities. Reaction of P3HT with singlet oxygen was monitored over a period of 16 h. The OD of the solution at 435 nm decreased by ~30%, whereas M_n of the polymer remained constant (Figure 7). Clearly chain scission does not originate from reaction with $^1O_2$ in contrast to photobleaching. FTIR analysis of the polymer following exposure to $^1O_2$ showed strong signals due to sulfine (1090–1020 cm^{-1}), keto (1730 cm^{-1}), and olefinic (1650 cm^{-1}) residues. Notably, no hydroxyl

Table II. Relative Rates of Photochain Scission and Photobleaching of P3HT in the Presence of Anthracene[a]

[anthracene] (M)	relative rates of photochain scission[b]	relative rates of photobleaching[c]
0.00	1.00	1.00
1.25×10^{-4}	1.10	0.52
2.50×10^{-4}	1.10	0.38
3.75×10^{-4}	1.10	0.26
5.00×10^{-4}	1.10	0.19
10.00×10^{-4}	1.10	0.20

[a] P3HT in $CHCl_3$ (1 mg/mL) at 25 °C. The incident wavelength was 435 nm. [b] Determined by GPC. [c] Determined from a decrease in OD of P3HT at 435 nm.

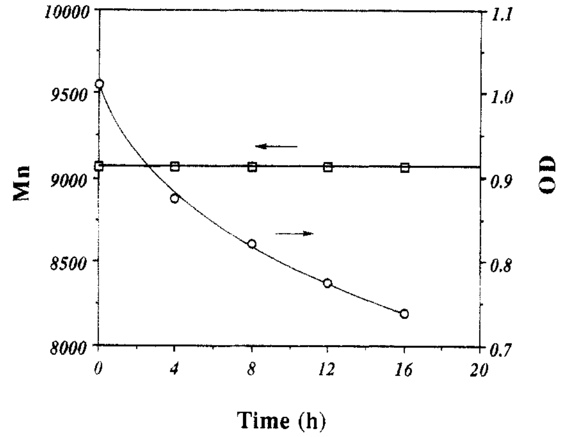


Figure 7. Decrease in the optical density (λ_{max} = 435 nm) and change in M_n of poly(3-hexylthiophene) in $CHCl_3$ (1 mg/mL) during reaction with chemically generated singlet oxygen.

functionality was observed (Figure 8). The slight change in the aliphatic C–H stretching band is attributed to the new chemical environment following ring opening.

Spectroscopic analyses of reaction products are consistent with reported mechanisms observed for the reaction of $^1O_2$ with small-molecule thienyls.[68,69] A similar mechanism has been postulated for longer chain thienyls.[21] In this mechanism, shown in Scheme I, $^1O_2$ undergoes a 1,4 Diels–Alder addition with thienyl units. Endoperoxide residues **2** may be envisaged as intermediate in the formation of sulfine. However, their formation as primary oxygenation products can only be inferred from the photochemical products because endoperoxides derived from heterocyclic 1,3-dienes are generally unstable at room temperature.[70] Highly unstable monomeric thiophene endoperoxides (thiaozonides) have been isolated however by reductive trapping with diazene at −78 °C[71] but decompose to the sulfine **3**, or the *trans*-diketone **4**. Spectroscopic analyses of reaction products between P3HT and singlet oxygen, and for photolyzed samples, are consistent with this mechanism.

The possibility of reaction between singlet oxygen and the alkyl side chain is highly improbable. Saturated polymers such as polyethylene and polypropylene are completely inert to singlet oxygen,[72] and the participation of singlet oxygen in the mechanism of photooxidation of more reactive polymers such as polystyrene is negligible. In fact polystyrene has been used as a matrix for studying the diffusion of $^1O_2$ in polymers[73] and for photooxygenation of polynuclear aromatic hydrocarbons.[74]

Photochain Scission. Since singlet oxygen alone is not responsible for chain scission and the products of reaction between singlet oxygen and thiophenes are photolytically inert,[75] a classical photooxidative route has been tentatively proposed.[21] Photooxidation of polyolefins is initiated by the photosensitization of free radicals by impurities such as residual transition-metal catalysts.[76–81] In experiments designed to elucidate the role of free radicals in the chemistry of P3HT, and independent source of radicals, namely, the thermolysis of *tert*-butyl peroxide,

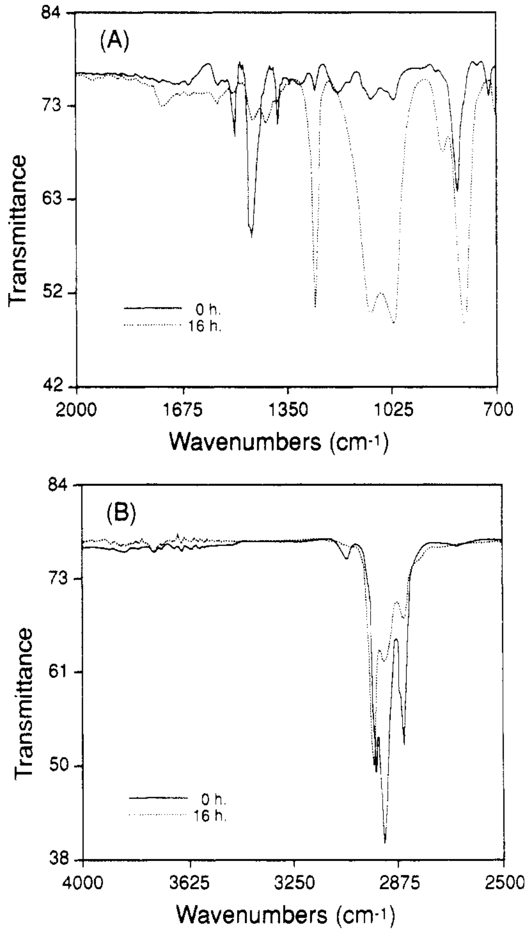


Figure 8. (A and B) FTIR and P3HT before (0 h) and after reaction with chemically generated singlet oxygen (reaction time, 16 h).

Scheme I

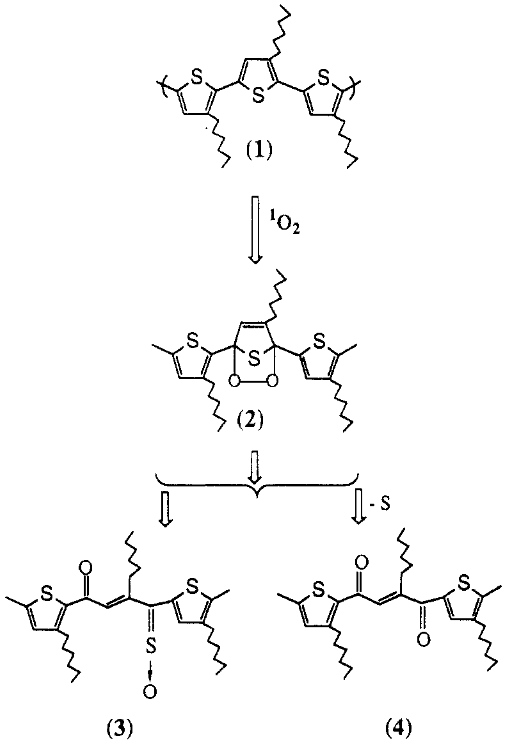


Table III. Rates of Photochain Scission and Photobleaching for Various Polymers[a]

synthetic method	[Fe][b] (wt %)	relative rates of chain scission[c]	relative rates of photobleaching[d]
$FeCl_3$	3.2	2.38	3.57
$FeCl_3$	1.38	2.00	2.26
$FeCl_3$	0.05	1.66	1.36
Grignard		1.31	1.28
electropolymn		1.00	1.00

[a] P3HT in $CHCl_3$ (1 mg/mL) at 25 °C. Incident wavelength, broad band, 300–500 nm. [b] Determined by AA. [c] Determined by GPC. [d] Determined from a decrease in OD of P3HT at 435 nm.

was used to successfully initiate chain scission in the absence of light. Molecular weights of the polymer in refluxing benzene/*tert*-butyl peroxide at 160 °C decreased from 8500 to 5000 over a period of 45 h, representing an average of ~0.8 chain scissions. In the absence of the free-radical source no decrease in molecular weight was found, clearly indicating the role of free radicals in chain scission. Over the same period of time the optical density of the polymer decreased by ~3% in the presence of *tert*-butyl peroxide.

The pristine polymer does not contain any obvious organic free-radical initiators, but, as a consequence of the synthetic procedure, residual inorganic salts remain as impurities even after extensive purification.[82–84] Mössbauer spectroscopic analysis indicated the main impurity as Fe^{3+}, which is consistent with previous reports.[85,86] Quantitative analysis using AA spectroscopy gave an iron(III) concentration in the polymer of 0.05 wt % (0.15 mol % based on the repeating unit). To test the hypothesis that photolysis of residual Fe salts are a source of free radicals, a polymer sample was prepared by oxidative coupling with $FeCl_3$ and subjected to various degrees of purification in order to provide different concentrations of iron(III) residuals (see the Experimental Section and Table III). In all cases Mössbauer indicated the presence of iron(III) only and polymers exhibited identical UV–vis absorption spectra. The corresponding relative rates of photochain scission were 1.0, 1.21, and 1.44 for samples containing iron concentrations of 0.05 wt % (0.15 mol %), 1.38 wt % (4.15 mol %), and 3.20 wt % (9.6 mol %), respectively (Table III). From the increases in rate a dependence on the residual iron(III) on chain scission is confirmed.

Further evidence for iron-induced photochain scission was gathered by comparing rates of chain scission with poly(3-hexylthiophenes) prepared using techniques for which iron species are not employed, namely, electropolymerization and the Grignard route. Comparative rates of change of photochain scission are given in Table III. The rates of chain scission for the lowest concentration of residual iron(III) are 1.7 and 1.3 times greater than those for electrochemically and Grignard synthesized analogs, respectively. The fact that polymers prepared by electropolymerization and by Grignard synthesis undergo photochain scission, albeit to a lesser extent than those prepared by ferric chloride, is not surprising since photolysis of residual oxyanons (XO_n^-) in electropolymerized samples can produce reactive atomic oxygen,[87] and residual metal iodide produced by the Grignard syntheses also leads to free radicals upon photolysis.[88]

Mechanism of Photochain Scission. When O_2 was vigorously removed from solution, no photochemistry or photochain scission was observed even after 20 h of photolysis through a 300-nm cut-off filter with a 150-W Hg lamp. A previous report describing a small but noticeable extent of photochain scission[20] is attributed to the presence of residual dissolved oxygen. Chain scission is solvent dependent and wavelength dependent.[20] The fact that quantum yields of chain scission are 12 times higher when the incident wavelength is 313 nm compared to 436 nm can be attributed to relative extinction coefficients of the polymer at these wavelengths.[89] The latter produces an inner filter effect at the longer wavelength and reduces the quantity of light transmitted to the iron(III) species. These trends strongly point to a photooxidative free-radical pathway in which the initial step is photolysis of FeX_3 (eq 2).[79,90] X is likely to be an

$$Fe^{3+}X^- \rightarrow [Fe^{2+}X^\bullet] \rightarrow X^\bullet \qquad (2)$$

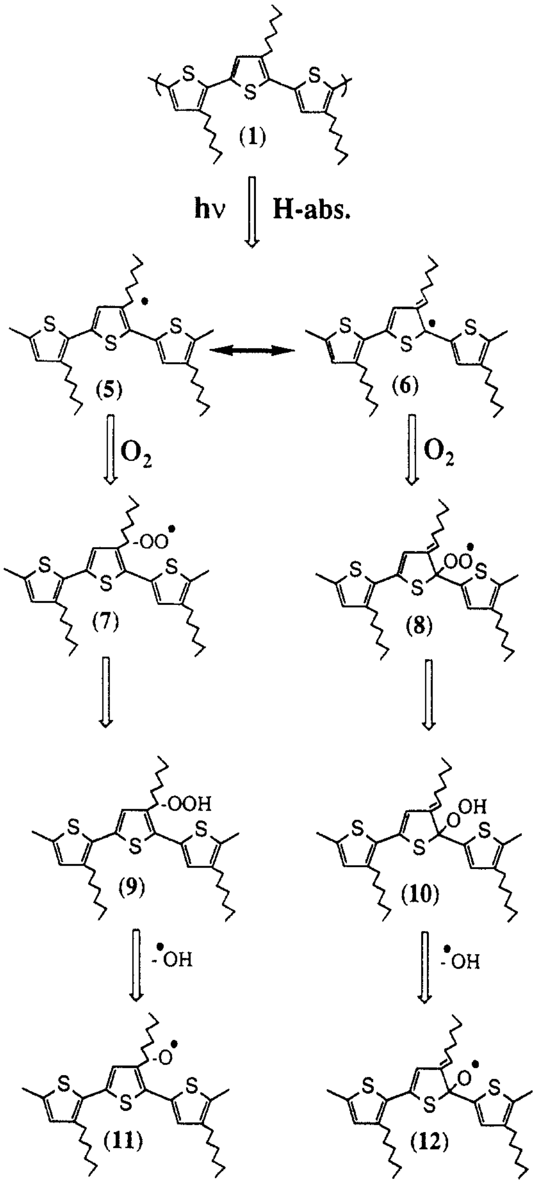
inert species such as OH. Chlorides are ruled out since $FeCl_3$ would act as a dopant which would be observed by UV–vis spectroscopy given that residual iron contents are as high as 9.6 mol % in some cases.

IR and NMR spectroscopies show that the alkyl side chain on polythiophenes plays an essential role in the photochemistry of P3HT. We propose that the primary point of attack by free radicals is the α-carbon atom of the hexyl group which results in H-abstraction. This is based on the lower dissociation energy of the α-C–H bond as a result of resonance stabilization of the radical. The mechanism is shown in Scheme II.

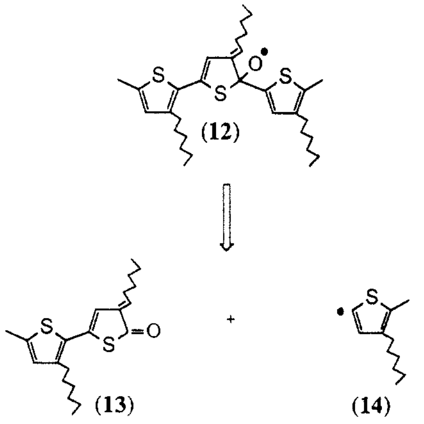
In this scheme the resulting P3HT radical is resonance stabilized by the π-system to yield radicals **5** and **6**.[91] Radicals **5** and **6** rapidly react with oxygen to produce peroxides **7** and **8** which can abstract a hydrogen from the polymer chain or solvent to give hydroperoxides **9** and **10**. Cleavage of the hydroperoxide group by light results in alkoxy radicals **11** and **12**. Fe^{2+} produced from reaction 2 might also take part in the cleavage of the OOH groups.[92] In this mechanism only rearrangement of the alkoxy radical **12** can cause chain scission with the formation of ketones **13** and thienyl radicals **14** (Scheme III). Alkoxy radical **11**, on the other hand, can undergo several of the following possibilities as shown in Scheme IV: (i) β-scission to yield an aldehyde **15** and volatile hydrocarbons; (ii) hydrogen abstraction to give a secondary alcohol **16**, (iii) radical coupling to form a cross-linked polymer. The latter possibility is suppressed in solution due to the low concentration of the polymer, but this pathway is viable in solid films.[5]

In the previous section we elucidated to the fact that photosensitization and reaction of singlet oxygen are primarily responsible for changes in the optical spectrum and photobleaching. However, examination of the data (Figure 6) obtained when anthracene was used as a singlet oxygen quencher, in the limit where increasing the quencher concentration did not impose any additional change in the rate of decrease of optical density, suggests an alternative minor pathway leading to photobleaching. This mechanism is believed free radical in nature. The increased rate of photobleaching with increasing residual iron content of the polymer (Table III) and the decrease in OD of the polymer solution upon thermolysis of *tert*-butyl peroxide is evidence of this. The possibility that residual optical bleaching is the result of chain scission and therefore due to a shorter contour length of the polymer can be ruled out since the absorbance characteristics of polythiophenes saturate at ~6 units while the degrees of polymerization for photolyzed polymers were considerably greater than this value. The mechanism of free-radical attack on the thienyl ring leading to a decrease in effective π-conjugation is yet undefined but can be considered as a minor pathway to photobleaching.

Scheme II

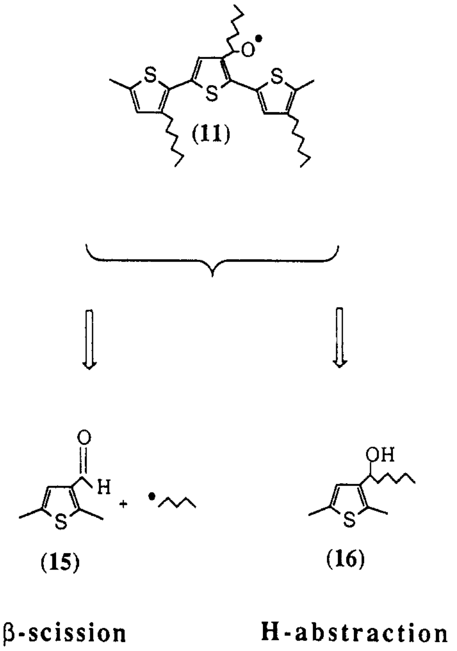


Scheme III



Chain scission

Scheme IV



Conclusion

Photobleaching of poly(3-hexylthiophene) in solution has been shown to occur in the presence of dissolved oxygen. The process involves photosensitization of singlet oxygen and its subsequent reaction with thienyl moieties by a 1,4 Diels–Alder addition. This mechanism of photobleaching can be suppressed by rigorous removal of O_2 or by trapping $^1O_2$ with quenchers. In the latter regard, 1,4-diazobicyclooctane (DABCO) might be a suitable choice of quencher due to the large rate constant of quenching[93] and due to the fact that DABCO is a physical quencher of $^1\Delta_gO_2$.[73]

A minor contribution to photobleaching arises from free-radical attack on the thienyl ring which reduces the extent of conjugation. Free radicals are formed when residual metal salts are photolyzed. In the presence of oxygen these radicals are also responsible for initiating a classical photooxidation pathway which culminates in chain scission.

The mechanisms of photodegradation of poly(3-hexylthiophenes) described in this work are believed applicable to the class of poly(3-alkylthiophenes) in general. This of course is restricted to P3AT's with alkyl chains longer than pentyl since the latter are generally insoluble. It appears that chain scission requires an α-CH_2 in the 3-position and would preclude poly(3-alkoxythiophenes) from exhibiting chain scission. However, photobleaching via the singlet oxygen route might still occur for these polymers. The results also provide a basis from which photochemical mechanisms in solid films of P3AT's can be deduced. The solid-state photochemistry of these materials is under current investigation.

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(60) Fluorescence from P3HT in solution is quenched by up to 50% in the presence of molecular oxygen.[21] Evidence suggests this quenching process does not lead to $^1O_2$ but may catalyze intersystem crossing to the polythienyl excited triplet state (Turro, N. J. *Modern Molecular Photochemistry*; Benjamin/Cummings: CA, 1978; Chapter 14). It is reasonable to propose that triplet thienyls in polythiophenes are responsible for photosensitization of $^1O_2$. However, it is worth noting that oxygen has virtually no effect on the fluorescence of α-terthiophene, suggesting major differences between the photophysics of oligomeric and polymeric thiophenes (see: Scaiano et al. Reference 59).

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