Chem. Mater. **1997,** *9,* 991−995

Photodegradation and Photostabilization Studies of Poly(3-butylthiophene) in the Solid State

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Received October 23, 1996. Revised Manuscript Received December 18, 1996⊗

A study to clarify the mechanism of the photochemical degradation of poly(3-alkylthiophene)s in the solid state was carried out. The isolation of two low molecular weight products allowed us to determine that the polymer, under irradiation of visible light, gives rise to singlet oxygen that will, in turn, cause oxidation of the polymeric chains. Furthermore, *N*-hexadecyl-*N*-methylaniline and 1-phenyldodecan-1-one were found to decrease the rate of polymer oxidation, the latter compound being more efficient than the former even at lower concentration. It is suggested the protective action by these substances may simply be due to their ability to act as a light screen.

Introduction

Conjugated thiophene based polymers have been intensely investigated due to their electrical and electronic properties and their potential applications.[1] The easy chemical or electrochemical polymerization and doping process along with the lightness of weight and the processability of these materials have stimulated interest in their possible use in electronic, communication, or information technologies.[2] Polythiophenes have been proposed as active components in energy storage applications,[3] in electrochromic devices,[4] in electrochemical sensors,[5] and in electronic devices such as photovoltaic[6] and photoelectrochemical cells,[7] FETs,[8] and light-emitting diodes.[9]

Poly(3-alkylthiophene)s and their oligomers have good electronic and mechanical properties:[10] they are processable from the melt or from solution and are quite stable environmentally. These features would allow their utilization in a variety of technologies involving thin films obtained by deposition from solution, by spin-coating, with the Langmuir−Blodgett technique and by ultrahigh-vacuum deposition.

The proposed use of poly(3-alkylthiophene)s in polymer-based light-emitting devices[11] appears problematic because, as with other polyconjugated macromolecules, these materials have low photochemical stability which leads to short operating lifetimes. The relevance of studies aimed at understanding the photodegradation mechanism is thus apparent.

Despite the fact that optical applications require thin films of poly(3-alkylthiophene)s, the photochemistry of these materials has been characterized in solution[12] but only scarcely in the solid state.[13] Hypotheses were formulated principally based on the study via FTIR and UV data. The conclusions were that either an adduct between oxygen and a thiophene ring of the π-conjugated chain is formed, generating carbonyl and sulfonic derivatives and breaking down the polythiophene backbone, or that alternatively the pathway may involve the side chain.[12]

In the present paper, the effect of additives on the stabilization or the destabilization of poly(3-alkylthiophene)s in the solid state under photochemical condition was also investigated. Poly(3-butylthiophene) (P3-BT, Figure 1) prepared via chemical oxidation with $FeCl_3$[14] was studied in terms of photooxidative stability of thin films, with and without the use of stabilization additives such as *N*-hexadecyl, *N*-methylaniline, and 1-phenyldodecan-1-one. The aim was to improve the polymer lifetime to photooxidation in optical devices. We were also able to isolate two products due to photooxi-

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⊗ Abstract published in *Advance ACS Abstracts,* February 1, 1997.

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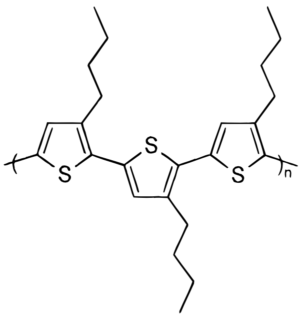

P3-BT

Figure 1.

dation that may clarify certain aspects of the oxidation mechanism of conjugated polythiophene chains.

Experimental Section

Instrumentation and Procedures. Irradiation experiments were carried out in a RPR-100 Rayonet photochemical reactor equipped with 16 F8T5/D and F8T5/CW lamps (8 W each) irradiating in the visible range (400−800 nm). UV−vis spectra were run on a Jasco UVIDEC 510 double-beam spectrophotometer in the range 350−650 nm. IR spectra were performed using a Perkin-Elmer System 2000 FT-IR casting films on a KBr support. Emission spectra were run on a Jasco FP-770 spectrofluorimeter, equipped with a phosphorimeter working at 77 K (liquid nitrogen) in EPA (ethyl ether, pentane, ethyl alcohol, 5:5:2 v/v/v) glass. Fluorescence spectra were measured at room temperature using chloroform as solvent. NMR spectra were recorded on a Bruker AC250 (250 MHz) using deuterochloroform as solvent and TMS as internal standard. HPLC analyses were carried out on a Bruker LC 42 using a SiO_2 column and 95:5 hexane:ethyl acetate as eluent; flow rate 0.8 mL/min. Mass spectra were obtained on a Perkin-Elmer RMU-60 instrument. The molecular weight distribution (MWD) of the copolymers was obtained with a modular size exclusion chromatography (SEC) system Waters (Milford, MA). The SEC system consisted of a 600E pump, a 717 autosampler, a 410 differential refractometer, and a 490E UV−visible detector. The column set was composed of four Waters Ultrastyragel (10^5−10^4−10^3−500 Å pore size). The experimental conditions consisted of tetrahydrofuran as mobile phase continuously purged with helium, 35 °C temperature, 1 mL/min flow rate, a sample concentration of 0.5 mg/mL, and a 200 μL injection volume. The calibration curve, polynomial third-order fit, was constructed by 14 narrow MWD polystyrene standards with a molecular weight ranging from 162 to 3.28×10^{-6} g/mol. The polymer films were prepared by spin-coating with an Electron Mec TRS 5V Spinner.

Polymerization and Sample Preparation. Chloroform (Aldrich, spectrophotometric grade) was dried by fractional distillation on P_2O_5 under nitrogen. Anhydrous ferric chloride (Fluka) was purified by the dehydrating method with thionyl chloride.[15] The 3-butylthiophene monomer was synthesized from 3-bromothiophene and *n*-butyl Grignard reagent using [1,3-bis(diphenylphosphino)propane]nickel(II) chloride catalyst.[16] The pure monomer has been obtained by fractional distillation under reduced pressure. The polymer was prepared via chemical oxidation with ferric chloride starting from a 0.1 M solution of the monomer and a 0.4 M chloroform suspension of anhydrous $FeCl_3$.[15] The reaction proceeded at room temperature for 3 h, and then the mixture was poured into methanol and washed several times in a hydrazine solution (1% in volume) in methanol. The polymer prepared in this way (95% yield) was extracted in Soxhlet apparatus with methanol in order to remove the residual oxidant and the oligomers. The polymer was dissolved in chloroform and insoluble products were removed by filtration. Then it was precipitated from a solution of hydrazine in methanol to eliminate traces of the catalyst. The polymer was extracted in a Kumakawa apparatus with hexane to remove the low molecular weights. The poly(3-butylthiophene) used for this photochemical study has a molecular weight M_w of 146 000 with a polydispersity M_w/M_n of 3.2, and was soluble in chloroform, toluene, and tetrahydrofuran.

The polymer samples for photooxidation studies were obtained from chloroform solution by spin-coating and film-casting techniques. The films were homogeneous, and their optical density ranged from 0.4 to 0.6 of absorbance measured at the maximum of the electronic absorption.

Irradiation experiments were performed on film samples deposited on the surface of Pyrex glass plates. Some of these plates were inserted inside Pyrex tubes, with atmospheres respectively of nitrogen, air, or oxygen.

N-Hexadecyl-*N*-methylaniline (HMA) was prepared by alkylation of *N*-methylaniline with 1-bromohexadecane in the presence of triethylamine. HME is an oil. Its mass spectrum shows the molecular peak at *m*/*e* 331.

1-Phenyldodecan-1-one (PDK) was prepared via Friedel−Crafts reaction adding the chloride of the dodecanoic acid to a suspension of benzene and $AlCl_3$; PDK is a white solid (mp 45−47 °C), and its mass spectrum shows the molecular peak at *m*/*e* 260.

Photostabilization studies were performed on film samples containing *N*-hexadecyl-*N*-methylaniline or 1-phenyldodecan-1-one. The polymer and different amounts of additive ranging from 2 to 20% in weight were dissolved in chloroform, and the mixtures were filmed on glass by spin-coating.

A selected number of glass plates were irradiated directly or in controlled atmosphere sealed tubes using a merry-go-round apparatus and removed at fixed times. Some of the samples were washed with hexane after irradiation, to remove soluble products produced during the photodegradation process. The hexane solutions were fractionated via thin-layer and HPLC chromatographies and allowed us to isolate two products, whose structures will be discussed later.

Results

Photochemical Reaction in the Solid State. The first studied reaction was the photooxidation of poly(3-butylthiophene) without additives in film samples deposited on Pyrex glass with the spin-coating technique. The polymer degradation was followed by electronic absorption spectroscopy in the range 360−650 nm. The UV−vis spectra of these films show an absorption band in the visible range corresponding to a $\pi-\pi^*$ transition whose energy depends on π-electron delocalization. The decrease of the mean conjugation length, possibly due to photooxidation reactions, can be easily monitored by the position of the absorption maximum and by the decrease of its absorbance.

Photoirradiation experiments of P3-BT were carried out under nitrogen, air, or oxygen atmosphere using lamps irradiating in the visible range. Substantial differences in the electronic spectra were found only when irradiation was performed in air or oxygen, showing that the polymer itself is photochemically stable in an inert atmosphere, while degradation occurs in the presence of oxygen. In Figure 2, a plot of the absorbance difference after and before photoirradiation ($A-A°$) vs irradiation time (t) is reported. The fact that no appreciable variation of the absorbance is detected under nitrogen means that no fragmentation of the polymeric chain occurs simply irradiating the polymer. Variations start to become appreciable only if oxygen is present indicating its active role. A plau-

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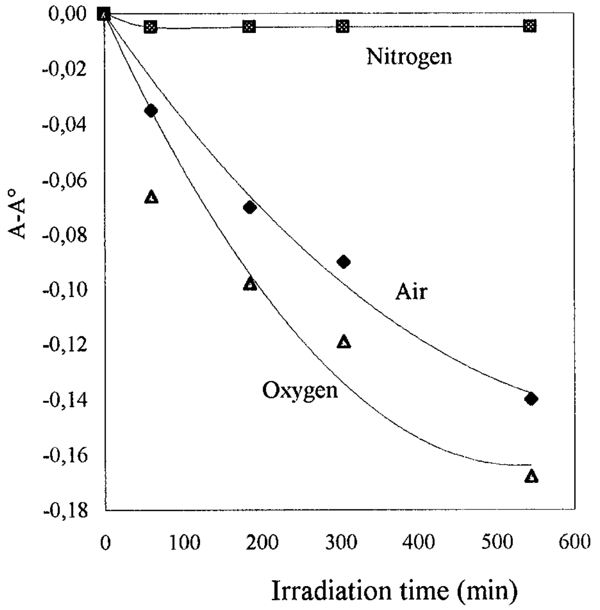
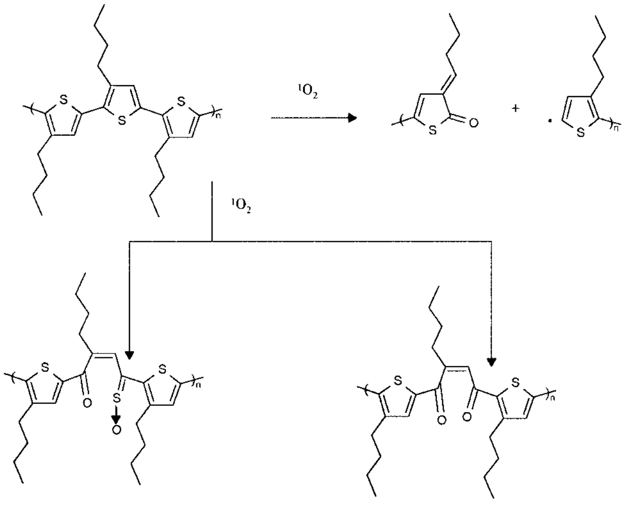


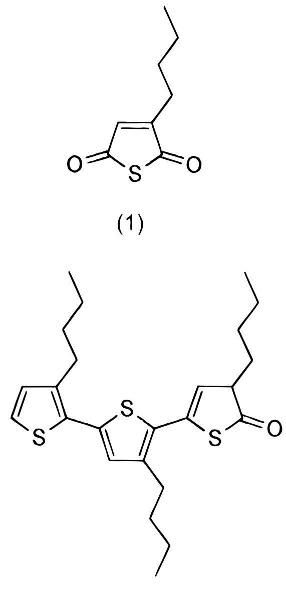
Figure 2. Absorbance difference vs irradiation time of P3-BT under nitrogen, air, or oxygen.

Scheme 1



sible mechanism of photooxidation is an energy transfer from the excited polymer to oxygen, forming singlet oxygen that in turn will react with the conjugated chain. This statement is in accordance with a recent report by Heeger et al.,[17] which confirmed the existence of the intersystem crossing in poly(3-octylthiophene); thus, this triplet state can transfer energy to oxygen forming singlet oxygen.

Recently the photodegradation of poly(3-alkylthiophenes) in solution has been studied by Holdcroft et al.[12] A degradation mechanism was inferred, and some oxidation products were proposed based mainly on FT-IR spectra of the irradiated solutions (Scheme 1). In the present investigation, a different approach was used since in the solid state the photodegradation of these materials may produce low molecular weight species that can be easily isolated and studied in order to clarify the mechanism of the process which may in principle be different than in solution. Because generally low molecular weight species have a better solubility in organic solvents, we have treated the irradiated films of poly(3-butylthiophene) with hexane to extract the soluble species present in the samples. A chromatographic separation allowed us to isolate small amounts of two low molecular weight compounds.


(1)

(2)

Figure 3. Structure of the products isolated after the photolysis of P3-BT under air.

The first molecule was identified as the thioanhydride **1** in Figure 3 from vibrational and electronic spectra and from mass analysis. The FTIR spectrum shows a series of bands (2960, 2924, and 2852 cm^{-1}) typical of the aliphatic stretching and similar to those of the starting monomer. Another band, absent in the spectrum of the original polymer at 1725 cm^{-1}, can be attributed to the CO stretching. The UV spectrum shows an absorption at 324 nm. These spectroscopical data are consistent with the characterization of the unsubstituted thioanhydride reported in the literature[18] for which the IR spectrum shows a band at 1730 cm^{-1} and the UV absorption maximum is at 318 nm. The mass spectrum of the product shows a 141 *m/e* peak corresponding to the highest mass fragment, but this peak cannot be interpreted as the molecular ion. It is noteworthy that the mass spectrum of the 3-butylthiophene monomer shows that the molecular mass peak is generally not detected, but only the fragment corresponding to the loss of the ethyl group is present. If we assume that a similar ethyl group loss from the molecular mass also occurred in our product, the total mass should amount to 170.

The second compound, that was obtained in higher amounts, shows in the FTIR spectrum a series of bands (2960, 2924, 2852 cm^{-1}) typical of the aliphatic stretching and similar to those of the starting polymer, while an additional weak band, absent in the spectrum of the original polymer, at 1732 cm^{-1} can be attributed to the C=O stretching. The ^{1}H NMR spectrum shows the aliphatic peaks in the ranges 0.8–1.0, 1.2–1.7, and 2.4–2.9 δ and the thiophene hydrogens in the range 6.7–7.5 δ but does not show the presence of vinyl or allyl

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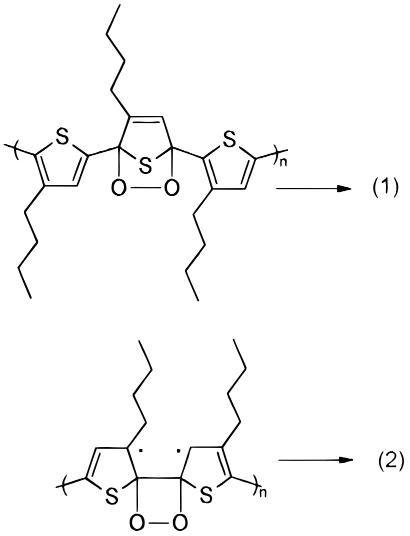
Scheme 2



hydrogens, indicating that the alkyl chains are still intact. The mass analysis gives a peak at *m/e* 432, while the UV spectrum shows an absorption band at 390 nm consistent with a substituted terthiophene (which shows a maximum at 360 nm). These findings bring us to structure **2** in Figure 3 as the most probable for our compound.

As far as the mechanism is concerned, we suggest that in the solid state singlet oxygen may add to the extended π system of the polymer and the products we isolate come from the competition between a 1−2 and 1−3 addition (Scheme 2). Subsequent fragmentations of these intermediates will generate our products. The radical produced in these reactions may give rise to recombination or attack to other chains forming complex derivatives. Indeed treatment of the irradiated plates with $CHCl_3$ (a solvent in which the original polymer is soluble) shows the presence of insoluble material, indicating that more complex polymer systems are present.

Photostabilization with Additives. The natural followup to our study of the photoreactions occurring at the polyenic chain was to attempt to identify substances able to slow, if not to block completely, the variation of the electronic spectra of irradiated poly(3-butylthiophene). Since in the literature, compounds that are normally used against oxidation were reported to have unsatisfactory effects,[19] we decided to investigate substances that were not used until now. *N*-Hexadecyl-*N*-methylaniline (HMA) and 1-phenyldodecan-1-one (PDK, Figure 4) were chosen because the former may react with oxygen, while the latter may absorb light and develop its own photochemistry.

The additive (HMA or PDK) was dissolved in a solution of PBT in chloroform, and the mixture was deposited on Pyrex glass by spin coating. Photoirradiation of the samples containing the additive was performed in air atmosphere, and the process was followed with UV spectroscopy monitoring the shift of the PBT band. The plots in Figures 5 and 6 show the effect of the addition of HMA and PDK, revealing striking differences between the two substances at least with wavelengths, concentrations, and time of irradiation used. While the protection by HMA depends on its concentration, the one of PDK seems rather insensitive to that parameter and in any case appears to give better results.

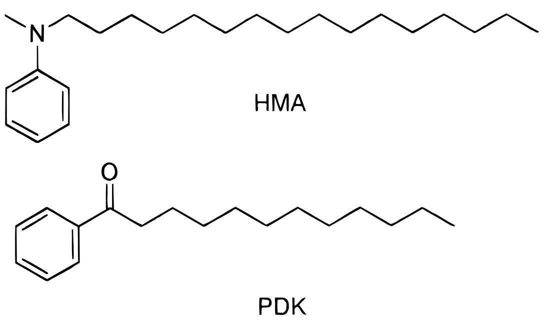


Figure 4.

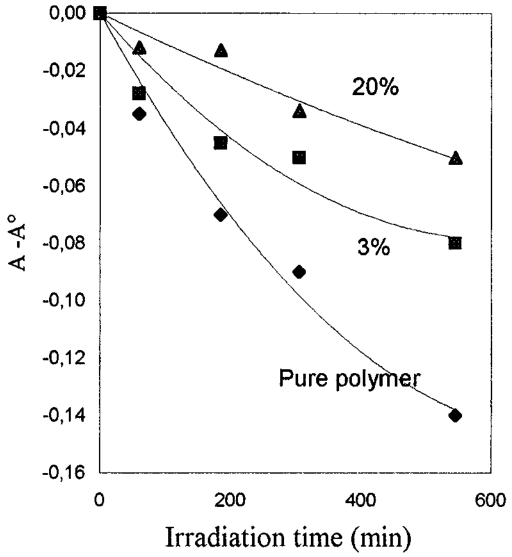


Figure 5. Absorbance difference vs irradiation time of P3-BT under air in the presence of *N*-hexadecyl-*N*-methylaniline (HMA).

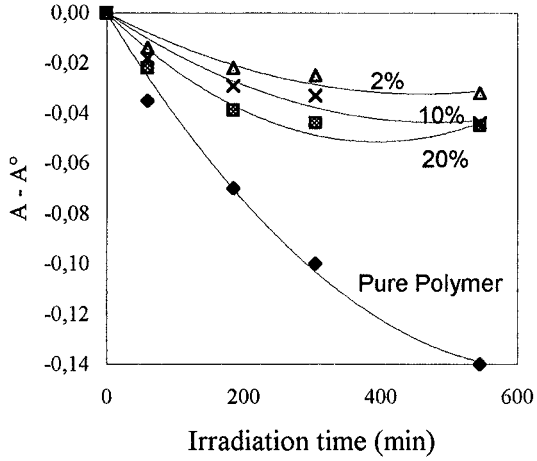


Figure 6. Absorbance difference vs irradiation time of P3-BT under air in the presence of 1-phenyldodecan-1-one (PDK).

To understand the mechanism of photostabilization of the additives and their difference as photoprotectors, we have studied the excited state of both the polymer and the additives, and we tried as well to isolate possible degradation products formed during photoirradiation.

The emission spectra of both polymer and additives allowed to determine the energies of their excited states

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Table 1. Singlet and Triplet Energies for P3-BT, HMA, and PDK

compound	singlet energy (eV)	triplet energy (eV)
PBT	2.58	
HMA	3.73	3.18
PDK		3.14

(Table 1). From these data, it is possible to exclude that the slowing down in the degradation is due to an energy transfer from the excited polymer to the additive, but rather the reverse may occur.

The irradiated samples of polymer containing also the additives have been treated with hexane to isolate the products due to the photodegradation of the additives. The treatment with the solvent of PBT thin film with HMA allowed us to recover the aniline derivative but none of its degradation products. In the case of the sample with PDK, acetophenone and dec-1-ene were isolated, showing that the Norrish type II reaction is operating. A hypothesis that can be put forward is that, with different efficiency, the aniline and the ketone additives act essentially as a light screen without transfer of energy to the polymer. A different mechanism cannot be ruled out in principle, but no supporting evidence is presently available.

To test the light-screen protection hypothesis and since substituted polythiophenes have been shown to be interesting materials for polymer-based light-emitting devices, we studied the effect of the PDK additive on the photoluminescence of poly(3-butylthiophene). The fluorescence spectra of PBT in solution without or with adding different amounts (from 2 to 50% by weight) of PDK were recorded. No differences were found either in the amount of the emitted light or in the position of the band. This is a clear indication that the electronic properties of poly(3-alkylthiophenes) are not affected by the presence of the 1-phenyldocecan-1-one.

Conclusions

Owing to the increasing importance of the practical applications of poly(3-alkylthiophenes), the identification of a photochemical stabilizer against their oxidation seems important. The present results appear even more promising, considering that the identified stabilizer does not affect the emission properties of the polymer.

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