CHEMISTRY OF MATERIALS
Article

Chem. Mater. 2011, 23, 145–154 145
DOI:10.1021/cm102373k

# Photodegradation of P3HT−A Systematic Study of Environmental Factors

Holger Hintz,[†] H.-J. Egelhaaf,*[‡] Larry Lüer,[§] Jens Hauch,[‡]
Heiko Peisert,[†] and Thomas Chassé[†]

[†]*Institute for Physical and Theoretical Chemistry, Eberhard-Karls-University, Auf der Morgenstelle 18, D-72076 Tübingen, Germany,* [‡]*Konarka Technologies GmbH, Landgrabenstrasse 94, D-90443 Nürnberg, Germany, and* [§]*Madrid Institute for Advanced Studies, IMDEA Nanociencia, Mòdulo 13; Avda Fco Tomas y Valiente, 7, 28049 Madrid, Spain*

*Received August 18, 2010. Revised Manuscript Received November 30, 2010*

The influence of environmental factors on the degradation process of P3HT film has been investigated quantitatively. The decay kinetics of the polymer absorption during variation of intensity and spectral distribution of the incident light, oxygen concentration, humidity level as well as temperature are monitored using infrared and UV/vis absorption spectroscopy. Additionally, the oxygen diffusion into the polymer film has been investigated using fluorescence spectroscopy under the same experimental conditions. The degradation process is light initiated with a strong increase of the effectiveness toward the ultraviolet region of the spectrum. The observed photo oxidation is not oxygen diffusion limited although an activation energy of 26 $\mathrm{kJmol^{-1}}$ was observed for both degradation and oxygen diffusion. The observed kinetics, especially its dependence on wavelength of the incident light, point to a radical-based degradation process in the solid state rather than a singlet oxygen-based mechanism as it is observed in the liquid phase. Furthermore the presence of humidity strongly affects the degradation process although water itself does not decompose the polymer. Changing the structure of the polymer from regioregular to regiorandom significantly accelerates the degradation, probably due to the higher triplet yield of the regiorandom polymer.

## 1. Introduction

The stability of polymeric semiconductor materials like poly-3-hexylthiophene (P3HT) is a key challenge that has to be faced in order to allow the commercial application in devices like organic solar cells and organic field-effect transistors. Although there are many polymers that show better performance in organic photovoltaic (OPV) devices, P3HT has still, by far, the highest commercial relevance in OPV. Moreover, it is among the polymers with the largest database on degradation and thus serves as a model system for degradation studies. P3HT contains neither vinylene bonds nor fluorene moieties and thus does not have obvious weak points as poly(paraphenylenvinylene)s and polyfluorenes have. Understanding of the degradation mechanisms of P3HT will make it possible to synthesize a broad variety of new polymers with enhanced stability. The exposure of P3HT to light and oxygen leads to the destruction of the $\pi$-conjugated system in both, solution and the solid state. In solution, the degradation is known to originate from the presence of singlet oxygen sensitized by the polymer.[1,2] However, the mechanistic situation in the solid state seems to be completely different from that in solution. Even at high concentrations of singlet oxygen, P3HT films are reported to remain undegraded.[3] Thus, the mechanism has been proposed to proceed via a radical pathway.[4,5] It has been suggested that the radical mechanism proceeds via the hydrogen abstraction at the $\alpha$ carbon of the alkyl side chain[6,4] with subsequent formation of hydrogen peroxide and oxidation of the aromatic and alkylic system, accompanied by cross-linking[6,7] and the formation of volatile species.[5] Besides these irreversible effects, the exposure of P3HT to photo-oxidative conditions results in partially reversible doping via a polymer-oxygen charge transfer complex,[8] as shown by several groups.[5,9−12] Despite the effort spent on understanding the degradation of P3HT in

---

*Corresponding author. E-mail: hegelhaaf@konarka.com.

(1) Abdou, M. S. A.; Orfino, P.; Holdcroft, S. *J. Am. Chem. Soc.* **1997**, *119*, 4518–4524.
(2) Koch, M.; Nicolaescu, R.; Kamat, P. V. *J. Phys. Chem. C* **2009**, *113*, 11507–11513.
(3) Manceau, M.; Rivaton, A.; Gardette, J.-L. *Macromol. Rapid Commun.* **2008**, *29*, 1823–1827.
(4) Manceau, M.; Rivaton, A.; Gardette, J.-L.; Guillerez, S.; Lemaitre, N. *Polym. Degrad. Stab.* **2009**, *94*, 898–907.
(5) Hintz, H.; Egelhaaf, H.-J.; Peisert, H.; Chassé, T. *Polym. Degrad. Stab.* **2010**, *95*, 818–825.
(6) Ljungqvist, N.; Hjertberg, T. *Macromolecules* **1995**, *28*, 5993–5999.
(7) Abdou, M. S. A.; Holdcroft, S. *Can. J. Chem.* **1995**, *73*, 1893–1901.
(8) Abdou, M. S. A.; Orfino, P; Xie; Deen, M. J.; Holdcroft, S. *Adv. Mater.* **1994**, *6*, 838–841.
(9) Seemann, A.; Egelhaaf, H.-J.; Brabec, C. J.; Hauch, J. A. *Org. Electron.* **2009**, *10*, 1424–1428.
(10) Seemann, A.; Sauermann, T.; Lungenschmied, C.; Armbruster, O.; Bauer, S.; Egelhaaf, H.-J.; Hauch, J. Solar Energy, **2010**, doi:10.1016/j.solener.2010.09.007
(11) Kendrick, C.; Semancik, S. *J. Vac. Sci. Technol. A* **1998**, *16.5*, 3068–3075.

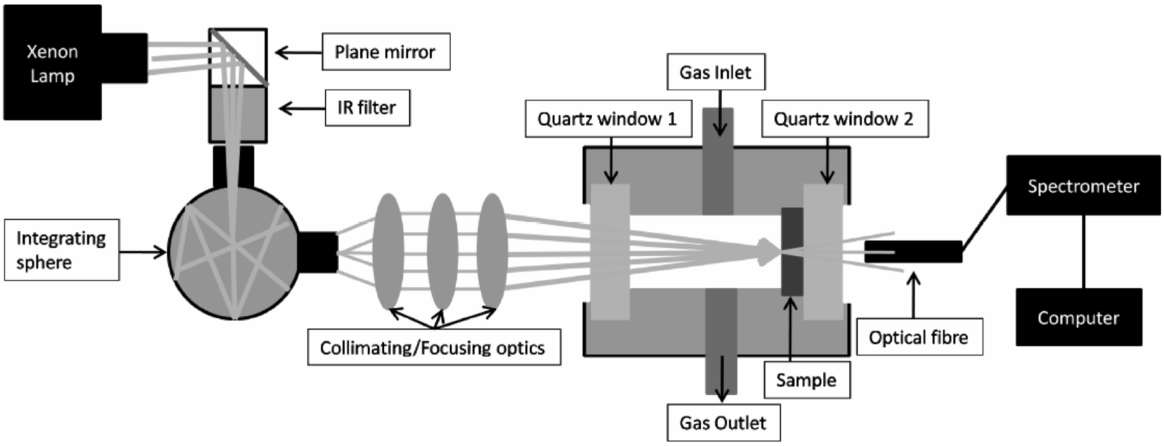


**Figure 1.** Reaction chamber and optical pathway of degradation and probe beam, respectively, used in the UV/vis measurements.

the solid state, there is still a lack of understanding of the details of the degradation mechanism. Literature reporting on the quantitative influence of illumination, temperature, and atmospheric conditions is rarely available, although these are key factors in polymer aging. In this work, the dependence of the photodegradation kinetics of P3HT films on irradiation intensity, wavelength, oxygen partial pressure, temperature, and humidity is investigated quantitatively by infrared and UV/vis absorption as well as fluorescence spectroscopy in order to obtain a broader data basis for the elucidation of the reaction pathways.

## 2. Experimental Section

**2.1. Preparation of Samples.** P3HT thin films (~100 nm in thickness as determined by atomic force microscopy and optical absorption measurements) were prepared under ambient conditions by doctor blading or spin coating on microscope slides using a 1% (w/w) solution of regioregular (Merck, number-average molecular weight 83 000 g mol$^{-1}$, weight-average molecular weight 113 000 g mol$^{-1}$; RR = 95%) and regiorandom P3HT (Merck, in chloroform (Uvasol, Merck). Thicker films of several micrometers were prepared via drop coating of a 1% solution on microscope slides. Prior to polymer deposition the substrates were cleaned in chloroform using an ultrasonic bath for 5 min. Thermal annealing of the samples was performed under nitrogen (170 °C, 30 min, N2 purity 5.0) in the dark. Afterward, the samples were transferred to the reaction chamber in the absence of light.

**2.2. Photoluminescence Quenching.** The diffusion coefficients of oxygen in thick films of P3HT (7 $\mu$m) were determined by monitoring the time trace of the oxygen induced fluorescence quenching with a Spex Fluorolog 222 spectrometer as described elsewhere.[13] To this end, the sample was placed in the reaction chamber with only short contact to ambient air in darkness (Figure 1). Subsequently, the chamber was evacuated (total pressure < 1 mbar) and finally flooded with oxygen (in less than 0.3 s, final pressure $p_{O_2}$ = 8 bar). During the measurement, the sample was continuously excited with monochromatic light at 550 nm and the fluorescence intensity was monitored at the maximum of the emission spectrum at 700 nm, correcting for fluctuations of the light source (< 2% of the total intensity) by using the signal of the reference photomultiplier of the Fluorolog 222. The temperature of the sample was adjusted using cartridge heaters attached to the sample cell and controlled by a Ni-NiCr thermocouple directly attached to the sample surface.

**2.3. Photo-oxidation of P3HT.** The photo oxidation experiments on P3HT thin films were carried out in a home-built reaction chamber under controlled oxygen partial pressures, humidity, and temperature measured by online sensors.

The reaction chamber and the optical path of the light used for degradation are described in Figure 1. The white light of a 450 W xenon high-pressure lamp is focused on the entrance port of an integrating sphere. Prior to the integrating sphere, the light passes a home-built infrared filter consisting of a quartz pipe filled with water (10 cm optical path) in order to reduce thermal stress to the following optical parts and the sample. Because of multiple diffuse reflectance of the incoming beam, the spatial intensity profile of the xenon arc vanishes; therefore a highly homogeneous intensity profile can be achieved, absolutely necessary for degradation experiments. The light leaves the integrating sphere and is collimated using several quartz lenses before being focused on the sample with a focus diameter of 10 mm. The sample cell can be operated under high pressure up to 11 bar, or in flow mode with 100 mL/min gas flow. Doing so, the ambient air is excluded. The transmitted light is then collected by an optical fiber connected to the UV/vis spectrometer therefore spectroscopic tracing of photo degradation is continuously possible. Monitoring of the oxygen partial pressure was done working with pure oxygen and a pressure sensor (Newport Omega PAA21R-V-10, error 1%) directly attached to the reaction chamber. The temperature was recorded attaching a self-made Ni/NiCr thermo pair (DIN 43710, error 1 K) directly on the sample surface using conductive silver. Different humidity levels were realized mixing dry (directly from the oxygen bottle) and wet (100 rel.hum. at 295 K) oxygen with different flow rates via a gas mixing facility. The humidity was monitored by positioning a calibrated sensor (Driesen & Kern company, DKRF400, 2% error) in the chamber and applying a constant flow of humidified oxygen and or synthetic air. Using a high-pressure Xenon lamp the intensity was adjusted to 0.13 Wcm$^{-2}$ recorded on the sample surface (maximum intensity achievable, integrated over the complete spectrum). This allows both accelerated and realistic illumination conditions. Illumination was performed from the polymer side to avoid spectral shielding effects by the substrate. Intensities were adjusted by inserting neutral density filters into the light path. A mercury

---

(12) Ogawa, S.; Naijo, T.; Kimura, Y.; Ishii, H.; Niwano, M. *Jpn. J. Appl. Phys.* **2006**, *45*, 530–533.

(13) Lüer, L.; Egelhaaf, H.-J.; Oelkrug, D.; Cerullo, G.; Lanzani, G.; Huismann, H.; De Leeuw, D. *Org. Electron.* **2004**, *5*, 83–89.

high-pressure lamp with attached monochromator was used to perform illumination with specific wavelengths in the range from 300 to 600 nm. Temperature, spectral light intensity, and humidity level were recorded in situ. Thus, the degradation was carried out under constant, controlled conditions, essential for mechanistic investigations.

**2.4. UV/Vis Spectroscopy.** UV/vis spectra were recorded in transmission mode using a homemade set up containing fiber optic spectrometers from ocean optics (Maya2000 pro and PC2000) both with a spectral resolution of approximately 3 nm. The time resolution was set between milliseconds (Maya2000pro, minimum 13 ms, PC2000, minimum 3 ms) and days, depending on the reaction rate. Determination of quantum yields was done by recording the photon density directly at the sample position using the spectrometer in absolute irradiance mode. To this end, the sample cell was placed in the degradation beam as in later experiments but without sample and quartz window 2 (Figure 1). Then an optical fiber equipped with a cosine corrector (both Ocean Optics) was positioned directly at the sample position in the reaction chamber. The optical fiber was connected to the calibrated Maya 2000 pro spectrometer. Calibration for wavelength resolved recording of the absolute light intensity was performed using a calibrated (NIST) white light source in the range from 200 to 1050 nm. Doing so it is possible to measure absolute, wavelength resolved photon fluxes on the sample surface that are not dependent on the spectral sensitivity of the detector.

**2.5. FT-IR Spectroscopy.** FT-IR spectra were recorded using a standard Bruker Vertex 66v spectrometer in transmission mode with a resolution of better than 1 $\mathrm{cm}^{-1}$. The base pressure of this vacuum spectrometer was better than 1 mbar. Samples were prepared on $CaF_2$ substrates in order to allow simultaneous investigation with UV/vis spectroscopy. Samples were transferred from the reaction chamber to the FTIR spectrometer with only short exposure times to ambient air (roughly 1 min), which were negligible compared to the observed reaction rates.

## 3. Results

### 3.1. Determination of Oxygen Diffusion Coefficient in P3HT Films by Fluorescence Quenching.

Upon admission of oxygen to a P3HT film, the fluorescence of P3HT is reduced by three different mechanisms, which take place on significantly different time scales: collisional quenching (in milliseconds to seconds, due to the encounter of polymer excited states with ground state oxygen), the formation of a CT complex between the polymer and oxygen (in minutes), as well as by photo-oxidation of the polymer (in hours).[13]

The fastest component of fluorescence quenching, which is due to collisional quenching, follows a Stern–Volmer behavior[13]

$$FQ = \frac{F_0}{F} - 1 = K_{SV}[O_2](t) \qquad (1)$$

where $F$ and $F_0$ are the fluorescence intensities with and without oxygen, respectively, $[O_2](t)$ is the time-dependent oxygen concentration, and $K_{SV}$ is the Stern–Volmer constant

$$K_{SV} = k_q \tau_0(S_1) \qquad (2)$$

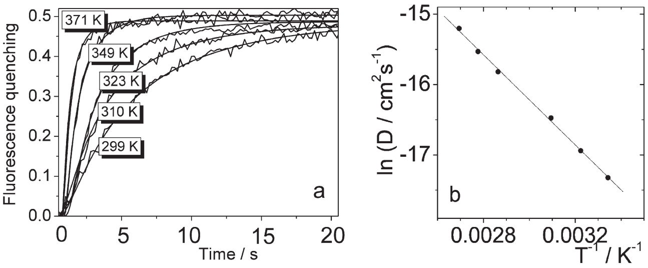


**Figure 2.** Temperature dependence of the diffusion of oxygen in annealed P3HT films. (a) Fluorescence quenching FQ in a 7 $\mu$m thick film of P3HT at different temperatures as a function of time after admission of oxygen ($p$ = 8 bar) at different temperatures: Lines, experimental data. Smooth lines, fits according to eq 1. (b) Arrhenius plot of the diffusion coefficients extracted from Figure 2a, according to eq 1.

where $\tau(S_1)$ is the unquenched singlet exciton lifetime and

$$k_q = 4\pi N_A R_{\mathrm{eff}}^{O_2}[D(S_1) + D(O_2)] \qquad (3)$$

is the quenching rate constant, containing Avogadro's number ($N_A$), the effective collision radius ($R_{\mathrm{eff}}^{O2}$, considering the possibility of finite quenching probability on the encounter of exciton and oxygen) and the sum of the diffusion coefficients of oxygen and the singlet exciton ($D(O_2)$ and $D(S_1)$, respectively). The facts that $FQ \propto [O_2]$ (from eq 1) and $D(S_1) \gg D(O_2)$,[13–15] allows the diffusion coefficient of oxygen in the P3HT film to be obtained by monitoring the temporal development of fluorescence quenching upon admission of oxygen into the evacuated sample chamber (Figure 2a). At an oxygen pressure of 8 bar, the fluorescence of annealed P3HT films of several micrometers in thickness is quenched by a factor of about two within a few seconds. Fitting the fluorescence quenching curves according to the diffusion model detailed in reference 13 we find an oxygen diffusion coefficient of $D(O_2) = 3 \times 10^{-8}\ \mathrm{cm}^2\ \mathrm{s}^{-1}$ at 295 K, which is close to the value reported by others.[1] The diffusion coefficient turns out to be independent of the presence of water, both for diffusion of oxygen into as well as out of the film. Even samples which have been stored under oxygen at 100% rel. humidity (295 K) for several hours show exactly the same rate of fluorescence recovery upon pumping of oxygen as do samples which have been stored under dry oxygen (see the Supporting Information). To determine the activation energy of diffusion, we determined the diffusion coefficient in the temperature range from $T$ = 293 K to $T$ = 100 K. From the Arrhenius plot in Figure 2b, an activation energy for oxygen diffusion of $E_A = 26.5 \pm 0.5\ \mathrm{kJ\ mol}^{-1}$ is obtained, which is a typical value for the diffusion of oxygen in polymers below the glass-transition temperature.[16–18]

Although the collisional component of fluorescence quenching (FQ) is completely reversible upon removal

---

(14) Kroeze, J. E.; Savenije, T. J.; Vermeulen, M. J. W.; Warman, J. M. *J. Phys. Chem. B* **2003**, *107*, 7696–7705.
(15) Shaw, P. E.; Ruseckas, A.; Samuel, I. D. W. *Adv. Mater.* **2008**, *20*, 3516–3520.
(16) Kaptan, H. Y. *J. Appl. Polym. Sci.* **1999**, *71*, 1203–1207.
(17) Horas, J. A. *J. Polym. Sci., Part B* **1996**, *34*, 1547–1553.
(18) Gao, Y.; Maca, A. M.; Wang, B.; Ogilby, P. R. *Macromolecules* **1994**, *27*, 7041–7048.

**Table 1. Absorbance Loss and Fluorescence Quenching (FQ) of a P3HT Film on Glass after Irradiation with the Full Spectrum of a 450 W Xe Lamp under 10 Bar of Oxygen for Different Times $t_{irr}$[a]**

| $t_{irr}$ (s) | absorbance | [*P*] (mM) | FQ | [*Q*] (mM) |
|---|---|---|---|---|
| 0 | 1.200 | 0 | 0 | 0 |
| 600 | 1.193 | 39 | 0.26 | 1.0 |
| 2400 | 1.179 | 144 | 0.46 | 1.8 |

[a] $c_P$ and $c_Q$ are the concentrations of photo-oxidized rings (as calculated from the absorption loss) and of fluorescence quenchers (as calculated from FQ), respectively. The films were excited at 550 nm, the fluorescence intensity was monitored at 700 nm (no spectral shift of the PL was observed during the measurement) and corrected for the intensity of the absorbed light.

of oxygen,[13] the slow component is only partially reversible. The reversible part of the slow FQ component is due to the light-assisted formation of a charge transfer complex between the polymer and oxygen,[1,8,13,19] whereas the irreversible part is due to photo-oxidation of the polymer[13] and is thus accompanied by a loss of absorbance. Obviously, a small loss in absorbance (by about 2%) leads to substantial photoluminescence (PL) quenching (by about one-third), see Table. 1. This is due to the diffusion of excitons to the quenching centers which have been formed by photo-oxidation of the polymer.[20] Assuming that Stern−Volmer kinetics not only apply to the quenching of fluorescence by oxygen but also to FQ by photo-oxidatively created defects, we can give an estimate for the concentration of quenching sites, [*Q*], by solving the Stern−Volmer equation

$$[Q] = \frac{\mathrm{FQ}}{4\pi N_A R^Q_{\mathrm{eff}} D(\mathrm{S}_1)\tau_0(\mathrm{S}_1)} \qquad (4)$$

Inserting typical values of $R^Q_{\mathrm{eff}} = 1 \times 10^{-9}$ m,[14,21] $D(\mathrm{S}_1) = 1 \times 10^{-7}$ m$^2$ s$^{-1}$,[13,15] and $\tau_0(\mathrm{S}_1) = 3.4 \times 10^{-10}$ s[13] for collision radius of quenching site and exciton, exciton diffusion coefficient, and exciton lifetime in the absence of quenchers, respectively, we obtain the quencher concentrations given in Table 1.

On the other hand, the concentration of thiophene rings which have been oxidized, [*P*], is obtained from the loss of UV/vis absorbance, $\Delta E_{\max}$, of a P3HT film of thickness *d*,

$$[P] = \frac{\Delta E_{\max}}{d\varepsilon_{\max}(T)} \qquad (5)$$

inserting a molar extinction coefficient per thiophene ring of $\varepsilon_{\max}(T) \approx 1 \times 10^4$ M$^{-1}$ cm$^{-1}$. This proportionality of absorbance loss and the number of destroyed thiophene rings is valid in the early stages of degradation in good approximation, irrespective of the degradation mechanism, because for long chains of thiophene units ($n > 10$) the spectral position of the absorption maximum depends only weakly on the conjugation length.[22]

Table 1 shows that the concentration of quenching sites increases monotonously with the progress of photo-oxidation. However, the absolute concentration of quenching sites as calculated from eq 4 is only a fraction of the concentration of oxidized thiophene rings obtained from eq 5, indicating that the reaction products are, on average, not very efficient quenching centers. Whether this is due to small effective quenching radii of the products, $R^Q_{\mathrm{eff}}$, or to small fractions of effective quenchers among the multitude of products, remains an open question.

**3.2. Photodegradation under Different Environmental Conditions.** UV/vis absorption spectroscopy is employed to quantify the effects of irreversible damage to the polymer films by irradiation under oxygen. As polymer films are also degraded by ozone[5,23] (produced, e.g., by the Xe lamp used for the experiments), the experiments were performed under controlled atmospheric conditions. In addition, the lateral spatial profile of degradation was verified to coincide with the intensity profile of the light spot on the sample. P3HT shows a broad absorption band in the visible region of the spectrum which shows two maxima at 520 and 554 nm, as well as a shoulder at 610 nm, the intensity of the latter increasing with the molecular order in the film.[24] Irradiation of a P3HT film with white light results in a steady decrease of the absorbance, together with a slight blue-shift of the absorption maximum (Figure 3). The transmittance in the nonabsorption region increases initially and decreases during the final stage of degradation. This change of transmittance is explained by changes in reflectivity, which are caused by a decrease of the refractive index[25] and of the thickness of the film. The decrease of the refractive index in the region of normal dispersion is due to the decrease of absorbance and to the blue shift of the absorption maximum. The decrease in film thickness has been observed in previous work by photoelectron spectroscopy[5] and is probably caused by the formation of volatile decomposition products.[5]

The time trace of the absorbance at the initial maximum at 554 nm shows a close to linear decrease during the initial phase of the degradation, which turns into an almost exponential decay toward the end of the degradation process. The degradation rate is taken as the initial slope of the reaction curve in Figure 2. For the degradation of a film of approximately 100 nm in thickness under 1 sun (AM1.5 conditions) and at an oxygen pressure of $p = 0.2$ bar, a degradation rate of $dE/dt \approx 1 \times 10^{-5}$ s$^{-1}$ is observed, *E* being the absorbance at 554 nm. Taking the contribution of one thiophene unit to the extinction coefficient at this wavelength as $\varepsilon = 1 \times 10^4$ M$^{-1}$ cm$^{-1}$, we obtain a photo degradation rate of $1 \times 10^{-12}$ mol cm$^{-2}$ s$^{-1}$

---

(19) Egelhaaf, H.-J.; Lüer, L.; Oelkrug, D.; Winter, G.; Haisch, P.; Hanack, M. *Synth. Met.* **1997**, *84*, 897–898.

(20) Yan, M.; Rothberg, L. J.; Papadimitrakopoulos, F.; Galvin, M. E.; Miller, T. M. *Phys. Rev. Lett.* **1994**, *73*, 744–747.

(21) Dicker, G.; de Haas, M. P.; Siebbeles, L. D. A.; Warman, J. M. *Phys. Rev. B* **2004**, *70*, 045203.

(22) Gierschner, J; Cornil, J.; Egelhaaf, H.-J. *Adv. Mater.* **2007**, *19*, 173–191.

(23) Chabinyc, M. L.; Street, R. A.; Northrup, J. E. *Appl. Phys. Lett.* **2007**, *90*, No. 123508.

(24) Brown, P. J.; Thomas, D. S.; Koehler, A.; Wilson, J. S.; Kim, J.-S.; Ramsdale, C. M.; Sirringhaus, H.; Friend, R. H. *Phys. Rev. B* **2003**, *67*, 642031–6420316.

(25) Arwin, H.; Jansson, R. *Electrochim. Acta* **1993**, *39*, 211–215.

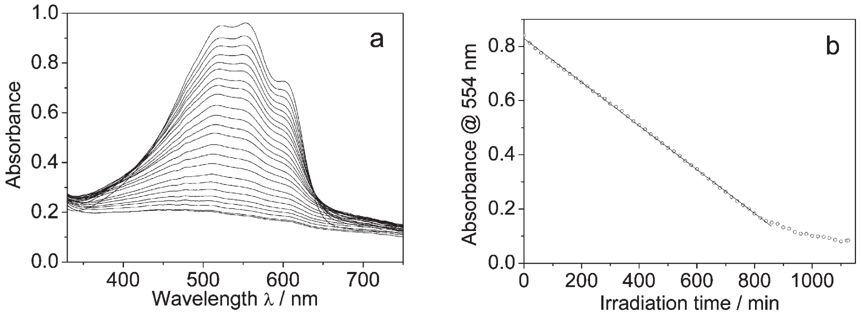


**Figure 3.** (a) UV/vis absorption spectra of a thin film of P3HT (initial thickness $d = 80$ nm) on glass during illumination with the spectrum of a focused 150 W Xe lamp under oxygen atmosphere ($I_0 = 0.13$ W cm$^{-2}$, $p = 11$ bar). (b) Time trace of the absorbance at 554 nm corrected by the baseline value at 700 nm extracted from the left panel.

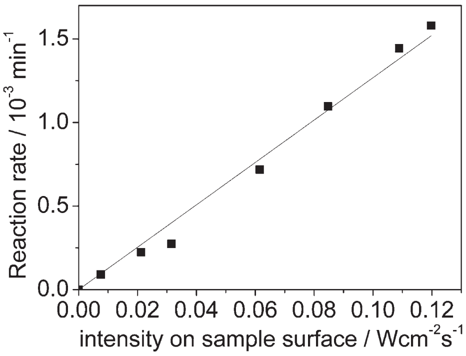


**Figure 4.** Degradation rate (monitored by the loss of absorbance at $\lambda = 554$ nm) of P3HT films by white light under 8 bar of dry oxygen as a function of light intensity (solid squares).

thiophene units. In the following, we will demonstrate how the degradation rate is affected by environmental parameters, such as light intensity, wavelength, temperature, oxygen partial pressure, and humidity.

*3.2.1. Variation in Light Intensity.* To determine the dependence of degradation rate on light intensity, P3HT films of comparable thicknesses ($d \approx 100$ nm) were irradiated with white light of different intensities in the range from $I = 0.08$ W cm$^{-2}$ s$^{-1}$ to 0.12 W cm$^{-2}$ s$^{-1}$ (maximum power output) at 8 bar oxygen partial pressure. Both the spectral distribution and the temperature were kept constant ($T = 298$ K, $\Delta T < 1$ K) over the whole investigated intensity range. The degradation rate depends linearly on the intensity incident on the sample (Figure 4) within the measured range. Degradation in the dark is negligible under our experimental conditions, as revealed by keeping films in the dark for 2 h at elevated temperatures and high oxygen pressures ($T = 373$ K, $p = 8$ bar oxygen) (not shown here).

*3.2.2. Wavelength Dependence of P3HT Photo Degradation.* So far all the investigations have been performed by irradiation with a broad band white light source. To further evaluate the role of the spectral distribution of the incoming light on the photo oxidation kinetics, we performed wavelength resolved degradation experiments. The wavelength dependence of the photo-oxidation rate is an important indication as to whether the polymer is destroyed by reacting with singlet oxygen which has been sensitized by the polymer itself or by a radical chain mechanism that is driven by the photogeneration of radicals by the photolysis of precursors absorbing in the UV region. In order to obtain the activation spectrum of photo-oxidation, polymer films were irradiated at different wavelengths, monitoring the decrease in UV/vis absorbance in-line. The activation spectrum of photodegradation, expressed in terms of effectiveness[26] $\mathscr{T}(\lambda)$, which is obtained from:

$$\mathscr{T}_\lambda = \frac{dN_{\mathrm{tr}}/dt}{I_{\mathrm{incident}}(\lambda)} \tag{6}$$

with $dN_{tr}/dt$ being the number of destroyed thiophene rings per unit area and time. $dN_{\mathrm{tr}}/dt$ is calculated from the decay of the absorbance $dE/dt$ at 554 nm and the molar absorption coefficient per thiophene ring $\varepsilon_{\mathrm{tr}} = 1 \times 10^4$ M$^{-1}$ cm$^{-1}$ according to

$$\frac{dN_{\mathrm{tr}}}{dt} = \frac{dE}{dt}\frac{N_{\mathrm{A}}}{\varepsilon_{\mathrm{tr}}} \tag{7}$$

$N_{\mathrm{A}}$ being Avogadro's number. The incident photon flux $I_{\mathrm{incident}}$ is recorded at the sample surface.

The validity of eq 7 requires the absorbance change, $\Delta E$, to be proportional to the number of oxidized thiophene rings, $\Delta N_{\mathrm{tr}}$. This proportionality has been demonstrated in a previous publication. By combining photoelectron spectroscopy (PES) and UV/vis spectroscopy in a previous work[5] it was shown that the absorption decay at 554 nm is linearly related to the PES sulfur signal corresponding to oxidized thiophene rings. Further support comes from the observation by us and by others[4] that the decay kinetics of the UV/vis absorption maximum and of the FTIR in the C═C double bond region show the same slope when normalized to the initial values.

The effectiveness of the P3HT photo-oxidation, which is obtained from eq 7 (Figure 5), increases toward the UV region, being by about a factor of 50 larger at 335 nm than at the main absorption maximum of the polymer around 550 nm. It is thus clearly different from the absorption spectrum of P3HT. Interestingly, it is similar to the activation spectra which have been observed for polymers with saturated backbones, like PE, PP,[27] PS,[28] and

---

(26) Andrady, A. L. *Adv. Polym. Sci.* **1997**, *128*, 48–94.
(27) Zhenfeng, Z.; Xingzhou, H.; Zubo, L. *Polym. Degrad. Stab.* **1996**, *5*, 93–97.
(28) Andrady, A.L. Final Report to U.S. EPA under Contract 68−02−4544, Task II-60, January 1991.

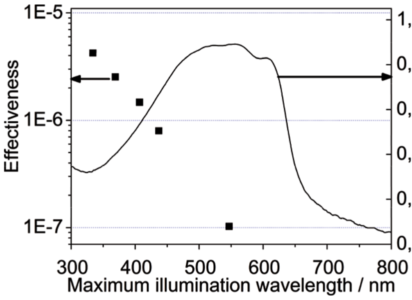


**Figure 5.** Effectiveness (squares) of the photo degradation of a P3HT film as a function of irradiation wavelength. The absorption spectrum of P3HT is shown as a solid line. Degradation experiments were performed under constant oxygen flow of 0.1 L min$^{-1}$ at 970 mbar oxygen partial pressure.

PMMA,[29] which are photo-oxidized by radical chain mechanisms.

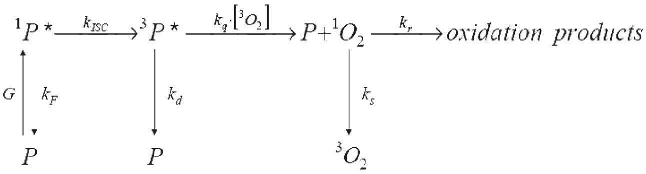
To check whether under white light illumination the oxidation rates at different wavelengths add up linearly or different wavelengths have a synergistic effect, we calculated the reaction rate under white light conditions from the wavelength resolved data (Figure 5). To this end, the spectral photon distribution of the illumination source (Xe high-pressure lamp), $I_0(\lambda)$ was multiplied with a fit to the photochemical quantum efficiencies (with respect to the incident photon flux $I_0(\lambda)$), $\phi_{\mathrm{pc}}(\lambda)$, as obtained from the monochromatic experiments (Figure 5). The integral of this function then yields the calculated reaction rate

$$v_{\mathrm{pc,calcd}} = \frac{dE}{\varepsilon_{\mathrm{T}} dt} = \int_{\lambda=0}^{\infty} \phi_{\mathrm{pc}}(\lambda) I_0(\lambda) d\lambda \qquad (8)$$

where $E$ is the absorbance of the film at the monitoring wavelength and $\varepsilon_{\mathrm{T}}$ the extinction coefficient of one thiophene unit at this wavelength. The reaction rate thus calculated and the experimental rate are in accordance within the error bars, thus showing that that the rates at different illumination wavelengths add up linearly.

*3.2.3. Thermal Activation of P3HT Photodegradation.* Temperature is another crucial environmental factor which has to be considered in the degradation of polymeric materials. The reaction rate of the photo-oxidation of P3HT films increases exponentially with temperature in the range from $T = 298$ to 393 K (Figure 6a). The activation energy obtained from the slope of the corresponding Arrhenius plot yields a value of $E_{\mathrm{A}} = 26$ kJ/mol (Figure 6b). As this value is equal to the activation energy found for oxygen diffusion in the P3HT films (see section 3.2.1.), the question arises whether oxygen diffusion might be the rate limiting step in the photo-oxidation of P3HT. However, at the conditions under which the temperature dependence is investigated ($p_{\mathrm{O}_2} = 6$ bar), the flux of oxygen into the film easily keeps up with the consumption of oxygen by the photo-oxidation. This becomes obvious when calculating the Deborah number $Z = L(D/k)^{-0.5} \approx 0.01$ from the thickness $L$ of the film, the diffusion coefficient of oxygen $D = 3 \times 10^{8}$ cm$^2$ s$^{-1}$ (see section 3.1) and the pseudo-first-order rate constant $k = -[\mathrm{O}_2]^{-1} \frac{d[\mathrm{O}_2]}{dt} = -[\mathrm{O}_2]^{-1} \frac{dA}{\varepsilon_{\mathrm{tr}} dt}$ of the photo-oxidation reaction, assuming that the absorbance loss equivalent to one thiophene ring corresponds to the consumption of one oxygen molecule.[5] The value of $Z = 0.01$ obtained for the Deborah number for films of about 100 nm in thickness indicates that the reaction rate is not controlled by the rate of oxygen diffusion into the film.[34] It also means that there should be no gradient of product distribution, which has been shown to be the actually the case in a previous publication.[5]

**Scheme 1. Kinetic Scheme of Polymer (P) Degradation by Polymer-Sensitized Singlet Oxygen**



*3.2.4. Dependence of the Photodegradation Rate on Oxygen Partial Pressure.* The dependence of the photo-oxidation rate on oxygen pressure is shown in Figure.7. For small oxygen partial pressures ($p < 0.2$ bar) the reaction rate increases steeply, whereas toward higher oxygen concentrations the rate asymptotically approaches the maximum value, which is about five times that of the value at the atmospheric oxygen partial pressure. Such a sublinear dependence of the degradation rate on oxygen partial pressure has been observed for several polymers, including LDPE[30] and dialkoxy-PPV.[31] It has been explained by different mechanisms, such as singlet oxygen sensitization[31-33] and radical chain mechanisms. For both mechanisms, the saturation of the rate for higher oxygen pressures is due to the depletion of a transient species by the reaction with oxygen or with an oxygen-centered radical species. Whereas in the singlet oxygen case the transient species is the triplet state of the polymer, it is a chain propagating radical (which reacts with an oxygen containing radical in the termination reaction) in the case of the radical mechanism.

The rate of polymer degradation by singlet oxygen (Scheme 1) is determined by the production of singlet oxygen in the collisional quenching of triplet states of the polymer by ground state oxygen

$$\frac{d[^1\mathrm{O}_2]}{dt} = k_{\mathrm{q}}[^3\mathrm{O}_2][^3P*] - (k_r[P] + k_{\mathrm{s}})[^1\mathrm{O}_2] \qquad (9)$$

The triplet state is formed from the singlet excited state and decays both spontaneously and because of the

---

(29) Andrady, A. L.; Searle, N. D.; Crewdson, L. F. E. *Polym. Degrad. Stab.* **1992**, *35*, 235–247.

(30) Papet G.; Audouin-Jirackova, L.; Verdu, J. Radiat. Phys. Chem. **1989**, *33*

(31) Staring, E. G. J.; Berntsen, A. J. M.; Romme, S. T. R.; Rikkeny, G. L. J. A.; Urbach, P. *Philos. Trans. R. Soc. London, Ser. A* **1997**, *355*, 695–706.

(32) Scurlock, R. D.; Wang, B.; Ogilby, P. R.; Sheats, J. R.; Clough, R. L. *J. Am. Chem. Soc.* **1995**, *117*, 10194–10202.

(33) Cumpston, B. H.; Jensen, K. F. *Synth. Met.* **1995**, *73*, 195.

(34) Audouin, L.; Langlois, V.; Verdu, J; de Bruin, J. C. M. *J. Mater. Sci.* **1994**, *29*, 569–583.

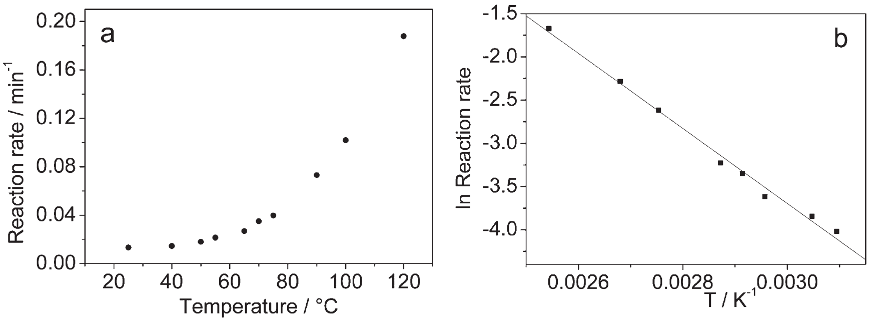


**Figure 6.** Temperature dependence of the photo-oxidation rate of annealed films of rre-P3HT under 6 bar of dry oxygen and at an irradiation intensity of $I_0 = 0.13$ W cm$^{-2}$. (a) Reaction rate vs temperature. (b) Arrhenius plot of the photo oxidation rates extracted from the left panel.

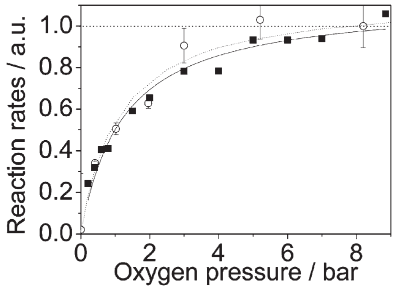


**Figure 7.** Normalized reaction rates as function of oxygen pressure (the value of the reaction rate at 8 bar is set to 1). Values obtained from UV/vis decay kinetics (554 nm, squares) and FTIR loss of carbon–carbon double bonds at 1509 cm$^{-1}$ (circles) are shown. The full and dotted lines are fits to the experimental data corresponding to eqs 11 (singlet oxygen mechanism) and 12 (radical mechanism), respectively.

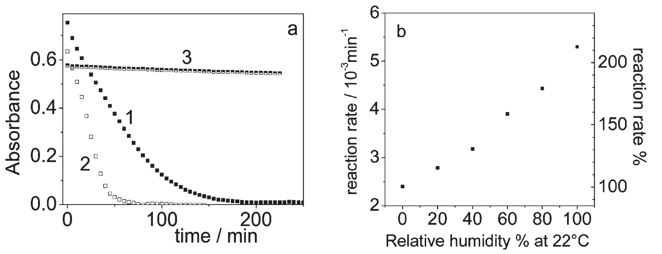


**Figure 8.** Effect of humidity on the photooxidation rate of annealed films of rre P3HT. a) time trace of the P3HT absorption maximum during degradation under (1) oxygen, (2) humidified oxygen (100% rel.humidity), and (3) humidified nitrogen (100% rel.humidity). b) Degradation rate as function of relative humidity at 295 K. Total pressure $p = 1$ bar in all experiments.

**Scheme 2. Kinetic scheme of polymer degradation by a radical chain mechanism (adopted from Audouin et al.[34])**

$$P \xrightarrow{G} P\bullet$$

$$P\bullet + {}^3O_2 \xrightarrow{k_2} PO_2\bullet$$

$$PO_2\bullet + PH \xrightarrow{k_3} PO_2H + P\bullet$$

$$P\bullet + P\bullet \xrightarrow{k_4} inactive\ species$$

$$PO_2\bullet + PO_2\bullet \xrightarrow{k_6} inactive\ species$$

quenching by ground-state oxygen

$$\frac{d[{}^3P^*]}{dt} = k_{\mathrm{ISC}}[{}^1P^*] - (k_{\mathrm{q}}[{}^3\mathrm{O}_2] + k_{\mathrm{d}})[{}^3P^*] \qquad (10)$$

In the steady state, the concentrations of the transient species are constant, so that the overall degradation rate is obtained as

$$-\frac{dP}{dt} = k_{\mathrm{r}}P^1\mathrm{O}_2 = \frac{G\phi_{\mathrm{ISC}}\phi_{\mathrm{r}}}{\left(1+\dfrac{k_{\mathrm{d}}}{k_{\mathrm{q}}{}^3\mathrm{O}_2}\right)} = \frac{G\phi_{\mathrm{ISC}}\phi_{\mathrm{r}}}{\left(1+\dfrac{k_{\mathrm{d}}}{k_{\mathrm{q}}Sp_{\mathrm{O}_2}}\right)} \qquad (11)$$

considering that the oxygen concentration in the film is given by the atmospheric pressure $P_{\mathrm{O}_2}$ and the solubility S. G is the generation rate of singlet excitons, $\phi_{\mathrm{ISC}}$ is the quantum yield of triplet population from the excited singlet state of the polymer, and $\phi_{\mathrm{r}}$ is the quantum efficiency of singlet oxygen deactivation by chemical reaction (as opposed to deactivation by physical deactivation). In the case of a radical chain mechanism (Scheme 2), radicals are formed in an initial step by irradiation. The chain is propagated in two subsequent steps, the first one involving oxygen consumption. Finally, the radical chain is terminated by the recombination of radicals.

In the steady state, the polymer is consumed at the rate[34]

$$-\frac{d[P]}{dt} = \frac{k_2(G/k_4)^{0.5}[{}^3\mathrm{O}_2]}{(k_2/k_3P)(k_6/k_4)^{0.5}[{}^3\mathrm{O}_2]+1} \qquad (12)$$

As evident from the fit curves in Figure 6, both functions describe the observed pressure dependence rather well, so that distinguishing between the two mechanisms on the basis of pressure dependence of the reaction rates is not possible.

*3.2.5. Accelerated Degradation in the Presence of Humidity.* Another environmental factor affecting the degradation rates is the ambient humidity (Figure 8a). The presence of humidity during the photo oxidation of P3HT increases the reaction rate significantly. Humidity in the absence of oxygen does not cause significant degradation, revealing that humidity itself is not responsible for the degradation of P3HT. The variation of relative humidity in the range from 0 to 100% (at 295 K) results in an increase in the reaction rate by a factor of 2.2 (Figure 8b). This value was consistently found for different oxygen

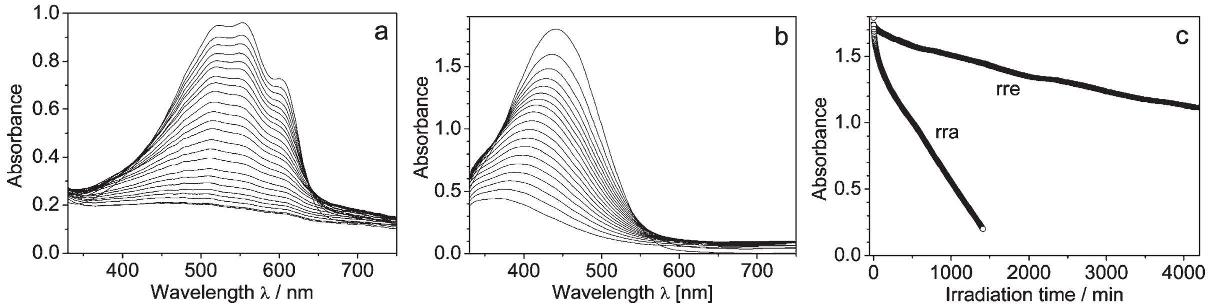


**Figure 9.** UV/vis spectra of (a) regioregular and (b) regiorandom P3HT thin films during photo oxididation. (c) Decay traces extracted from the UV/vis spectra of regioregular (554 nm) and regiorandom (442 nm) P3HT corrected by the baseline values at 800 nm.

partial pressures in the range from 0.2 bar to more than 3 bar.

*3.2.6. Structure of the Polymer and Morphology.* Finally, the structure of the polymer has to be considered. Both the shape of the UV/vis absorption band and the degradation rate depend sensitively on the structure of the polymers (Figure 9). While regioregular P3HT absorbs with the maximum located at 554 nm and shows a shoulder at 600 nm that is indicative for the lamellar arrangement of the polymer chains,[24] regiorandom P3HT shows an unstructured absorption band peaking at 442 nm. Under identical degradation conditions, regiorandom (rra-)P3HT is photo-oxidized much faster (by a factor of about five) than regioregular (rre-)P3HT (Figure 9c). The peak maximum of the rra-P3HT shifts to lower wavelengths much faster than in the case of the rre polymer.

Annealing films of P3HT of the same regioregularity (95%) does not have a measurable effect on the photo-oxidation rates (Figure 10a) although the films show clearly different absorption spectra, indicating that the annealed film has a significantly higher degree of crystallinity than the nonannealed film (Figure 10b). This is in good accordance with the results obtained in section 3.2.3, thus ruling out a diffusion limitation of oxidation and the absence of a spatial reaction gradient.

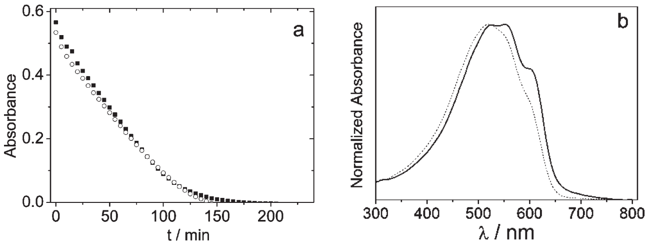


**Figure 10.** Effect of crystallinity of films of rre-P3HT. (a) Degradation kinetics for highly crystalline P3HT (full squares) and P3HT of lower crystallinity (open circles). (b) UV/vis spectra of highly crystalline P3HT (full line) and less crystalline P3HT (dot line).

## 4. Discussion

The degradation kinetics described above and their dependencies on environmental factors are summarized sufficiently well by the empirical expression

$$-\frac{dE}{\varepsilon_{\mathrm{T}}dt} = -\frac{dn_{\mathrm{T}}}{Adt} = \frac{\mathscr{T}(p_{\mathrm{O}_2} \to \infty, \lambda, T)I_0(\lambda)}{1 + b(T)p_{\mathrm{O}_2}^{-1}} + c(p_{\mathrm{O}_2}, T) \qquad (13)$$

where $E$ represents the absorbance of the film, $\varepsilon_{\mathrm{T}}$ the extinction coefficient of one thiophene unit, $A$ the unit area, $n_{\mathrm{T}}$ the number of moles of thiophene rings, $I_0$ the incident photon flux, $p_{\mathrm{O}_2}$ the oxygen partial pressure. $\mathscr{T}$ is the effectiveness as defined in eq 6, $b$ and $c$ are constants, $T$ is the temperature, and $\lambda$ is the irradiation wavelength. Typical values for these constants for a film of about 100 nm in thickness are $\mathscr{T}(p_{\mathrm{O}_2} \to \infty$, 334 nm, 300 K) $\approx 9 \times 10^{-6}$ mol Einstein$^{-1}$ and $b$(298 K) = 1.24 bar. Interestingly, $\mathscr{T}$ increases with the initial film thickness. Thermolysis of P3HT (and likewise of poly(arylenevinylene)s[35]) at moderate temperatures ($T <$ 400 K) under air in the dark, described by constant $c$, is negligible as compared to the photo-oxidative degradation of rre P3HT, even at low light levels.[4] Similarly, photolysis in the absence of oxygen[36] takes place on the time scale of years. Thus we will concentrate solely on the kinetics of photo-oxidation. Equation 13 is consistent with both mechanisms under discussion, the singlet oxygen path (eq 11) and the radical based pathway (eq 12). During degradation under constant oxygen partial pressure, the rate is also constant, i.e., the reaction is of zeroth order with respect to polythiophene (except for the very end of the reaction where the decay becomes approximately exponential). In other words, the reaction rate decreases neither with the absorbance of the film nor with the rapid decay of luminescence intensity, implying that the reaction rate does not depend on the concentration of excited states of the polymer. Consequently, the reaction rate does also not depend on the concentration of any species, e.g., singlet oxygen, which might be photosensitized by energy transfer from the polymer. There are several possible reasons why the degradation could be of zeroth order with respect to the polymer. First of all, the photo-oxidation might be a surface reaction. This would require at least one of the reactants, i.e., either the excited polymer or oxygen, to be restricted to the surface.

---

(35) Gustaf Winroth, S. B.; Rusli Daik, W. J.; Feast, F. C. *Org. Electron.* **2010**, *11*, 1445–1448.

(36) Manceau, M.; Chambon, S.; Rivaton, A.; Gardette, J.-L.; Guillerez, S.; Lemaître, N. *Sol. Energy Mater. Sol. Cells* **2010**, *94*, 1572–1577.

This is not very likely, as the penetration depth of light is on the order of the film thickness and the reaction is not limited by the diffusion of oxygen into the bulk, as pointed out above. Second, only the terminal thiophene rings of the polymer chains might be attacked. This would also explain the small blue-shift of the absorption maximum during photo-oxidation. A further possible reason for the zeroth order kinetics is that the reaction is initiated by the photolysis of an indestructible impurity or of an intermediate species, whose concentration is constant during most of the reaction. With the experimental results at hand it cannot be decided what is actually the reason for the observed zeroth order kinetics. Nevertheless, the zeroth order kinetics, i.e., the independence of the reaction rate on the absorbance of the polymer, is fully in accordance with the dependence of $\mathscr{T}$ on the wavelength of the incident photons, i.e., the activation spectrum of photo-oxidation. The activation spectrum of photodegradation increases continuously toward the UV region of the spectrum and is thus clearly different from the absorption spectrum of the P3HT film. Although the activation spectrum cannot be assigned to any specific chemical species, it excludes the sensitization of singlet oxygen by the polymer as the rate limiting step of the photo-oxidation. Consequently, a photoinduced radical-based pathway is the more likely degradation mechanism of rre P3HT under light and oxygen. This has already been suggested by Abdou and Holdcroft,[7] who identified radical induced cross-linking of the polymer chains as a major reaction pathway. More recent investigations[3] confirm this picture by showing that P3HT films are not attacked by singlet oxygen. Results from photoelectron spectroscopic investigations on the photo-oxidation kinetics of P3HT[5,37] further support a radical mechanism by demonstrating that alkylic and aromatic carbons are oxidized simultaneously, whereas singlet oxygen is reported to react preferably with the unsaturated carbon backbone of the polymer.[1]

The dependencies of the reaction rate on light intensity, oxygen pressure, and humidity are consistent with both mechanisms, radical chain and singlet oxygen degradation. The linear dependence on light intensity (Figure 4) indicates that the steady-state concentration of the active species is proportional to the rate of absorbed photons. However, this active species does not originate from excited states of the (intact) polymer, as this would neither be in accordance with the observed zeroth order kinetics nor would it agree with the activation spectrum of photo-oxidation in Figure 5. It also excludes that the bimolecular recombination of photogenerated radicals (Scheme 2) plays an important role in the overall reaction scheme. The pressure dependence of the degradation rate (Figure 7) indicates that oxygen or an oxygen centered intermediate species depletes a transient species involved in the rate limiting step of the reaction. This transient species may be either an excited state or a chain propagating radical species. Water in itself does not react with P3HT at significant rates, but acts as a promoter for the photo-oxidation of P3HT films (Figure.8). The question whether it acts as a solvent facilitating the diffusion of reactants (although it has no effect on the diffusion of oxygen), whether it stabilizes polar or ionic intermediates or whether it takes part in the reaction itself is the subject of ongoing investigations.

The structure of the polymer dramatically influences the degradation process (Figure 9). Regiorandom P3HT degrades by about a factor of 5 faster than its regioregular isomer. Its UV/vis absorption spectrum also exhibits a significant blue-shift during degradation (by about 100 nm), which is not observed for rre-P3HT, suggesting that the fragmentation of the conjugated $\pi$-system in rra-P3HT takes place in a more random fashion than in rre-P3HT, thus producing a random distribution of $\pi$-conjugated fragments whose average shifts to shorter conjugation lengths throughout the degradation process, very similar to what has been observed for the singlet oxygen driven photo-oxidation of P3HT in solution.[1] The different degrees of regioregularity have several consequences on the properties of the films, such as higher mobilities of the polymer chains and low-molecular-weight species, etc. The most striking difference of the two isomers lies in their grossly different triplet yields. While films of the regioregular isomer are reported to have triplet yields of $\phi_T < 1 \times 10^{-3}$, the regiorandom polymer shows significantly higher triplet yields[38] that might even approach the solution value of $\phi_T \approx 0.7$.[39] As oxygen diffusion is not rate-limiting, as shown above, and triplet states are photochemically much more active than singlet excited states, because of their longer lifetime, the higher triplet yield is most probably the reason for the accelerated photo-oxidation of the regiorandom polymer. A possible pathway of triplet-induced photo-oxidation might be the sensitization of singlet oxygen (see Scheme 1), which has been shown to be the species responsible for the photo-oxidation of P3HT in solution.[1,2]

## 5. Conclusion

In summary, we have performed an extensive investigation about the quantitative influence of several environmental factors on the photo oxidative degradation process of P3HT thin films. Although the experiments presented here involve only neat P3HT films, their implications also pertain to polymer:fullerene blends that are used as the photoactive layers in organic photovoltaic devices. Fullerenes have been shown to enhance the stability of most polymers, due to their action as excited state quenchers and radical scavengers,[36] but they do not completely stop photo-oxidation.

In practical terms, the simultaneous exposure of P3HT based electronic devices to oxygen and UV light will lead

---

[37] Manceau, M.; Gaume, J.; Rivaton, A.; Gardette, J.-L.; Monier, G. & Bideux, L. Thin Solid Films, **2010**, in press

[38] Österbacka, R.; An, C. P.; Jiang, X. M.; Vardeny, V. *Science* **2000**, *287*, 839–842.

[39] Seixas de Melo, J.; Burrows, H. D.; Svensson, M.; Andersson, M. R.; Monkman, A. P. *J. Chem. Phys.* **2003**, *118*, 1550–1556.

to fast irreversible deterioration of device performance. Even small extents of irreversible oxygen uptake ($\approx 3 \times 10^{-5}$ mol $O_2$, corresponding to 3.4 mL of air per gram of polymer) cause significant damage, as demonstrated by PL quenching experiments. The short-term exposure of devices to only one of the stress factors described above will cause only little irreversible damage,[35,36] whereas the careful exclusion of oxygen, humidity, and UV light by appropriate packaging is required for reliable long-term operation.

For rre-P3HT, our data support a radical-based degradation mechanism that is driven by UV light and accelerated by increasing humidity and temperature. Photo-oxidation is significantly enhanced for P3HT of low regioregularity, probably due to a change in the photophysics, namely an increase of the triplet yield, with decreasing morphological order of the films. The improved understanding of the degradation mechanisms of P3HT is essential in increasing the intrinsic stability of polymers for organic electronics, either by avoiding structural "Achilles' heels" in their design or by blending them with appropriate stabilizing additives.

**Acknowledgment.** We are grateful to W. Neu for technical support. This work was financially supported by the German Ministry for Education and Research (BMBF project "OPVStability", FKZ03SF0334).

**Supporting Information Available:** Additional information and images (PDF). This material is available free of charge via the Internet at http://pubs.acs.org.