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On the photochemical stability of dialkoxy-PPV; a quantitative approach

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In this paper we describe a quantitative approach to the photochemical degradation of a soluble dialkoxy-PPV that was also used to make polymer light-emitting diodes. We have defined a quantum yield for degradation (γ) and investigated the dependence (γ) on various experimental parameters, e.g. wavelength and power of incident light, and the dependence on the oxygen concentration. In the presence of oxygen the main degradation mechanism is photo-oxidation.

1. Introduction

Electroluminescent polymers are very promising candidates for application as active, emissive materials in a future generation of large area, thin and flat light sources. Areas of application include backlighting for LCD displays and structured (matrix or segmented) electroluminescent displays. Initial application will be in monochrome electroluminescent displays of limited resolution, e.g. 64×256, but in the future multicoloured and pixelated displays of higher resolution for video and computer monitors might also be possible. The most challenging and tempting application is certainly in electroluminescent devices, which are made on flexible substrates, offering the possibility of thin and flexible displays.

Poly(p-phenylenevinylene) (PPV) and its derivatives are among the most intensely studied materials for electroluminescence (Burroughes *et al.* 1990; Braun & Heeger 1991; Zhang *et al.* 1993; Doi *et al.* 1993; Burn *et al.* 1992*a*, *b*; Baigent *et al.* 1994; Greenham *et al.* 1993). A wide range of PPV derivatives has been described, offering opportunities to control the colour of the emission over the whole visible range of the spectrum (Braun *et al.* 1994) and allowing processing into thin films by solution processing (Staring *et al.* 1994, 1995). Devices based on these materials typically show external efficiencies of several percent, and a brightness of some $100 \, \mathrm{Cd \, m^{-2}}$ at low voltages, around 3 V. Most of the literature available on the subject, with few exceptions (Burrows *et al.* 1994), report on the initial performance of the EL devices. Getting to acceptable operating lifetimes for these devices represents one of the major challenges in the area of polymer electroluminescent devices.

PPV itself, and the derivatives are not very stable materials and several reports have appeared on the photochemical instability of PPV derivatives (Cumpston & Jensen 1995; Cumpston *et al.* 1997; Scott *et al.* 1996; Scurlock *et al.* 1995) or on the

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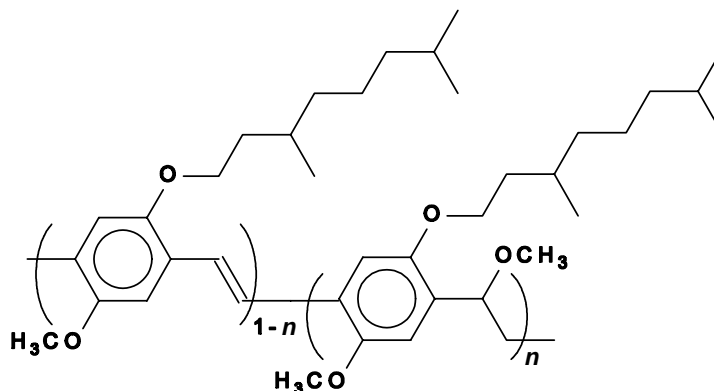
Figure 1. Structure of the partially conjugated OC_1C_{10}-PPV, used in these experiments.

oxidation of precursor PPV (Papadimitrakopoulos *et al.* 1994; Papadimitrakopoulos *et al.* 1994; Yan *et al.* 1994) in the conversion to conjugated material. Photochemical degradation of PPV is quite often photo-oxidation, but also other types of photochemical processes in PPV may lead to degradation. The formation of an excited state by absorption will lead to radiative or non-radiative decay to the ground state, in a ratio which is the photoluminescence efficiency, but may also induce photochemical reactions, e.g. inducing *cis-trans* isomerization of the vinylene-moiety, and even to cyclization, as observed in the case of stilbenes. This type of photochemical reaction might eventually be the determining factor for operating lifetime for devices that do not degrade because of oxidation, or degradation of the polymer electrode interface, or other external factors.

In this paper we describe the first results on the study of the quantitative approach to the photochemical stability of a soluble, dialkoxy substituted PPV, OC_1C_10-PPV (figure 1), that is partially conjugated. It is highly likely that other dialkoxy-substituted PPV derivatives, like the well-known MEH-PPV (Braun & Heeger 1991; Cumpston *et al.* 1997), will behave identically or at least very similarly.

2. Quantum yield for photodegradation, γ

In order to compare the stability of various polymers we need to find a measure for the stability. If a well-defined method to determine the photochemical stability is derived, we will be able to predict a lifetime for the polymer when it is used as the emissive layer in an electroluminescent device as well.

For a quantitative description of the photodegradation process we define quantum yield for photodegradation, γ, being the inverse of the average number of photons a molecule can absorb before being destroyed. An elegant method to measure this quantum yield was proposed by Boyarskii (1989). This method consists of irradiating the material and monitoring the increase of the transmission of this bleaching beam. This process can be analytically modelled and the experimental results fitted to the theory, the only adjustable parameter being γ.

The analysis is based on the following formulae. We consider the irradiation with an incoming Gaussian laser beam (width r) along the z-axis, perpendicular to the plane of the polymer film of thickness d (figure 2). The local absorption coefficient $\alpha(z, r, t)$ is determined by the local concentration of intact molecules N at depth z
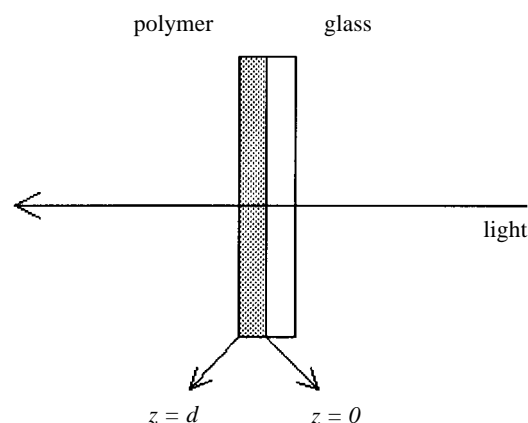
Figure 2. Schematic representation of sample geometry.

in the film, at a distance r from the centre of the laser beam, at all times during the experiment, $N(z, r, t)$:

$$\alpha(z, r, t) = \sigma N(z, r, t),$$

where σ is the absorption cross-section. $N(z, r, t)$ decreases in time through photochemical bleaching as given by

$$\frac{\partial N(z, r, t)}{\partial t} = -\gamma \sigma N(z, r, t) I(z, r, t),$$

where γ is the quantum yield for bleaching, whereas the decrease in excitation intensity I along the propagation direction, z, is given by

$$\frac{\delta I(z, r, t)}{\delta z} = -\sigma N(z, r, t) I(z, r, t).$$

In the previous equations it is assumed that the molecules resulting from the degradation process do not absorb at the laser wavelength. The boundary conditions for the intensity of the incident laser beam are

$$I(z = 0, r, t) = I_0 e^{-r^2/r_0^2} \equiv I_0(r),$$

where r_0 is the Gaussian beam waist, and

$$N(z, r, t = 0) = N_0.$$

This set of coupled partial differential equations can be solved. Without going into the details of the mathematical approach, $I(z, r, t)$ can be recovered:

$$I(z, r, t) = \frac{I_0(r)}{1 + (e^{\sigma N_0 z} - 1) e^{I_0(r) \sigma \gamma t}}.$$

The time dependence of the transmission through the film is

$$T(t) = \frac{\displaystyle\int_0^\infty I(z = d, r, t) r \, dr}{\displaystyle\int_0^\infty I(z = 0, r, t) r \, dr} T_\infty.$$
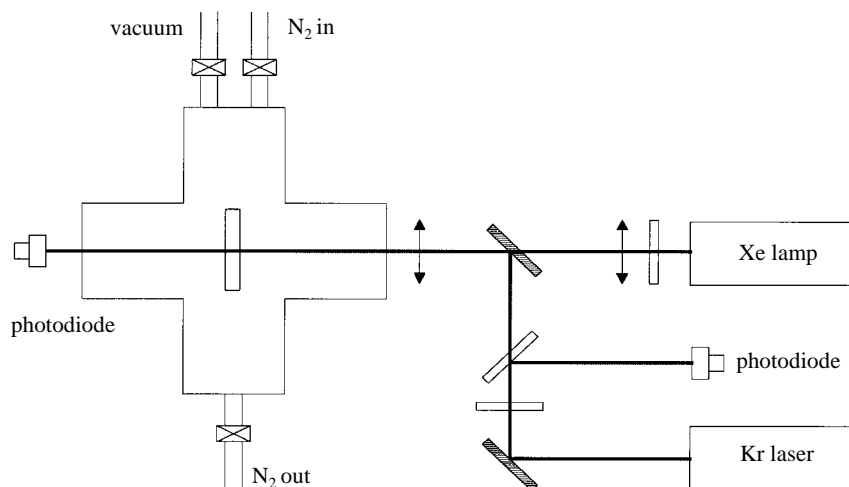
Figure 3. Experimental setup.

From which one deduces

$$T(t) = \frac{T_\infty}{I_0 \sigma \gamma t} \ln \left(\frac{T_0 e^{I_0 \sigma \gamma t} - T_0 + T_\infty}{T_\infty} \right),$$

where $T(t)$, T_0 and T_∞ is the transmittance of the sample at a certain time, at $t = 0$ and at the end of the bleaching process, respectively. T_0 and T_∞ can be measured directly. Before bleaching $\sigma = \alpha_0/N_0 I_0$ is the intensity of the incident laserbeam. The initial absorption coefficient α_0 is polymer and wavelength dependent. By measuring T_0 for different film thicknesses, α_0 can be calculated using

$$T_0 = T_\infty e^{-\alpha_0 d}.$$

3. Experimental setup

For our experiments, a thin film of the polymer is spincoated onto a glass substrate, and, from the glass side, illuminated with a laser beam of known intensity distribution, power and wavelength (figures 2 and 3). The sample is mounted in a chamber that can be pumped to a pressure below 10^{-6} mbar. Valves are used for the inlet of oxygen, nitrogen, air or any other gas. For illumination, a Kr laser, which can produce light of different wavelengths, or, as an alternative, a Xe lamp is used. The laser beam is guided by mirrors via an attenuation filter to the chamber. The transmitted and reflected light intensities are measured by the transmission and reflection diode, respectively. In order to monitor the bleaching intensity of the laser beam, 10% of the power is deflected, measured by the reference photodiode and used as reference signal. The signals from the photodiodes are measured with picoampere meters and the data are stored by a computer. Bleaching of the film occurs, with a rate that is measured by monitoring the transmission of the sample as a function of time. We assume that the absorption α is caused by a number of absorbing species ('a monomeric unit in the polymer backbone') with absorption cross-section σ. From the rate of bleaching, and from the intensity distribution of the incident laser beam in the sample (lateral variation due to beamwidth, depth variation due to bleaching
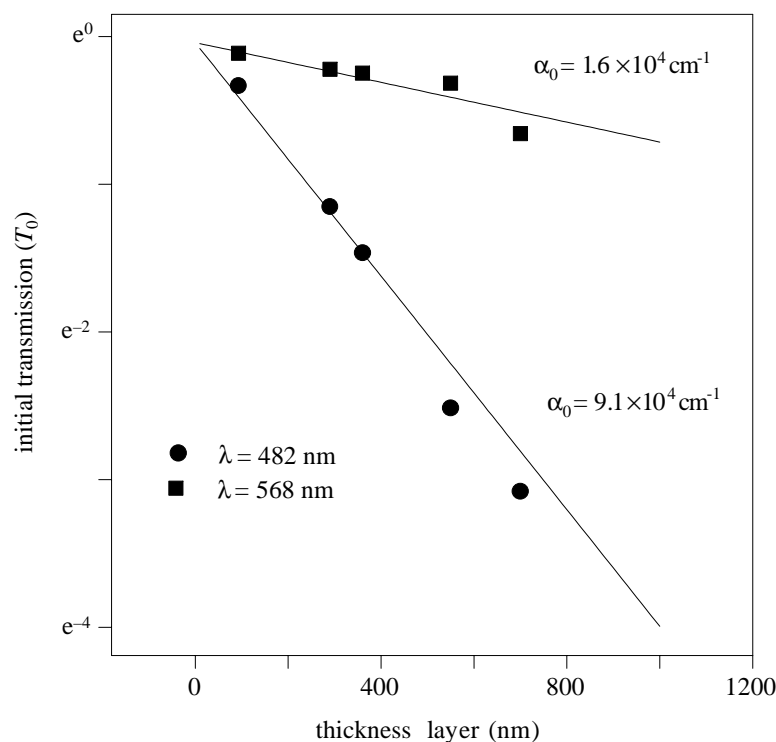
Figure 4. The initial transmission versus the thickness of the spincoated OC_1C_{10}-PPV film, at different wavelengths.

Table 1. *Material characteristics to determine g for OC_1C_{10}-PPV*

	ρ (g cm^{-3})	M (g mon^{-1})	N_0 (mon cm^{-1})^3	α_0 (cm^{-1})	σ (cm^2)
OC_1C_{10}	0.71	4.8×10^{-22}	1.47×10^{21}	9.1×10^4	6.2×10^{-17}

and absorption), one can deduce a quantum efficiency of bleaching γ. The model we use is not completely correct. For example, we do not take into account the absorption that is caused by products of the photodegradation, nor have we identified the exact nature of the absorbing species, we simply assume it to be 'a monomeric unit' in the polymer chain. Nevertheless, our model allows us to make comparisons of the photochemical stability of electroluminescent polymers of various structures.

Figure 4 shows the initial transmission versus the thickness of the polymer layer for different wavelengths. The circles represent the measured transmission for different OC_1C_{10}-PPV layer thicknesses, measured at a wavelength of 482 nm. The squares show the measured data at a wavelength of 568 nm. The solid lines in the figure are fitted to the measured data points. The initial absorption coefficient for $\lambda = 482$ nm is 9.1×10^4 cm^{-1} and for $\lambda = 568$ nm, $\alpha_0 = 1.6 \times 10^4$ cm^{-1}. The initial concentration of intact monomers, N_0, of the polymer can be calculated from the density, r, and the mass of a monomer, M (table 1).

The laser beam has a Gaussian profile as is described. In order to obtain a value for
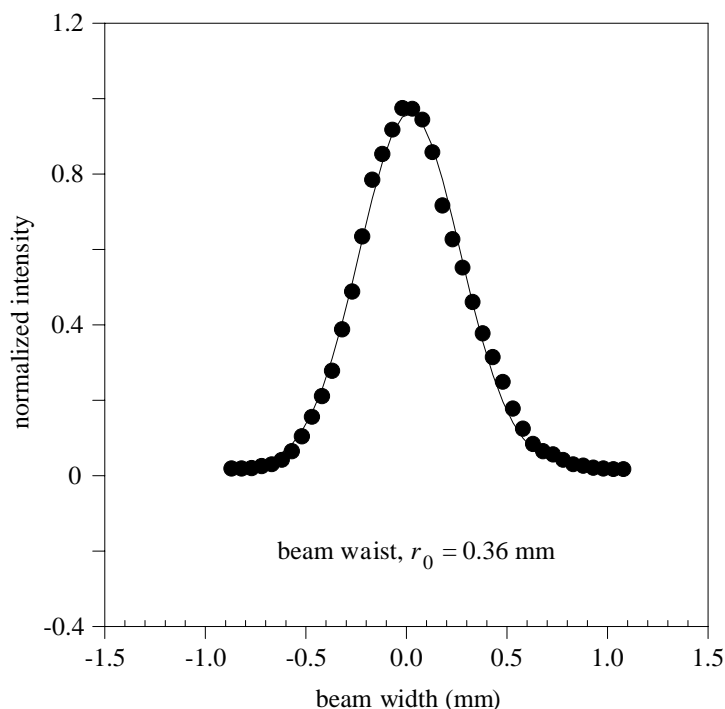
Figure 5. The intensity profile of the laser beam, fitted to a Gaussian profile. The datapoints
are measured by scanning a pinhole through the laser beam.

I_0 (photons cm^{-2}) we measure the total power of the laser beam, which is related to
I_0' (J cm^{-2}) and the Gaussian beam waist, r_0. The Gaussian beam waist is measured
by scanning a pinhole through the laser beam. The measured data is then fitted
to a Gaussian profile, see figure 5. The desired value for I_0 (photons cm^{-2}) is now
obtained by dividing I_0' by the photon energy of the particular wavelength.

4. Determination of γ

The result of one of the experiments is shown in figure 6. The dashed line shows the
measured transmission versus time for a 300 nm thick, 88% conjugated OC$_1$C$_{10}$-PPV
($n = 0.12$) film on a glass substrate. Irradiation was performed in air using the 482 nm
line of a Kr ion laser. The transmission increases strongly in the first 200 s, which
is caused by the photobleaching of the polymer, and saturates for longer bleaching
times. The reflection is almost constant in time ($R = 0.11$). If we consider the
transmission for longer bleaching times and add the constant reflection, we conclude
that almost 10% of the impinging laser light is not transmitted, nor reflected. This
10% is due to absorption and diffuse reflection of the cell.

In order to determine the quantum yield γ for bleaching, the experimental result
is fitted to theory, using only γ as the adjustable parameter. The fit thus obtained
is shown in figure 6 as the drawn line. The theoretical fit to the experimental curve
is excellent. The resulting value for the quantum yield for bleaching for OC$_1$C$_{10}$-
PPV with a laser wavelength of 482 nm is 1.1×10^{-4}. This means that the average
OC$_1$C$_{10}$-PPV monomer can absorb, $1/\gamma = 9.1 \times 10^3$ photons before it is bleached.
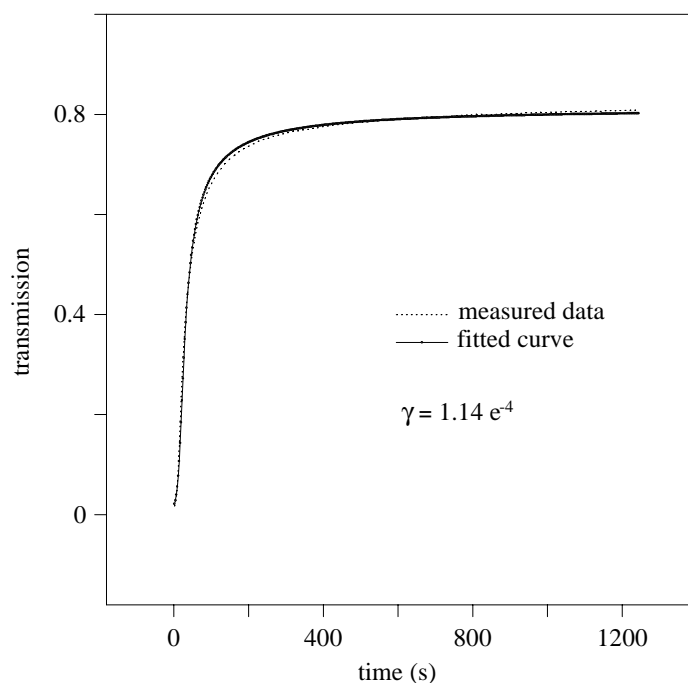
Figure 6. Measured and fitted transmission curve versus irradiation time for a 300 nm thick, 88% conjugated OC_1C_{10}-PPV ($n = 0.12$) film on a glass substrate.

These measurements were performed in air, and in FTIR spectra of the samples at various stages of the bleaching process we have seen a decrease of the intensity of the IR bands from C=C bonds, and an increase of the C=O bonds. This indicates, as observed by others previously, a cleavage of the vinylic bonds, and formation of aldehydes, and/or carboxylic acid derivatives, as was observed by Cumpston (1995, 1997) and by Scott (1996).

5. The bleaching power density dependence of γ

In order to find out whether γ is dependent on the bleaching power density for a wide range of power densities, the γ for samples with various thicknesses are determined over a power density range of almost three orders of magnitude. Figure 7 shows the fitted γ, at 482 nm, for OC_1C_{10}-PPV samples with thicknesses of 300 nm and 100 nm over a power density range of 158 mW cm^{-2}–55.2 W cm^{-2}, while keeping the beamwaist constant. We see that in that range the fitted γ are almost independent of the power density of the bleaching laser beam.

A different way to alter the power density is to change the beam waist of the laser, while keeping the total power constant. No dependence of the beam waist for γ was found in that experiment either.

We conclude that the proposed method to determine a measure for the stability by fitting the transmission curve versus time is reproducible and reliable over a wide range of bleaching power densities, within a margin of approximately 20%. Preliminary experiments on other polymers have indicated that the stability of structurally
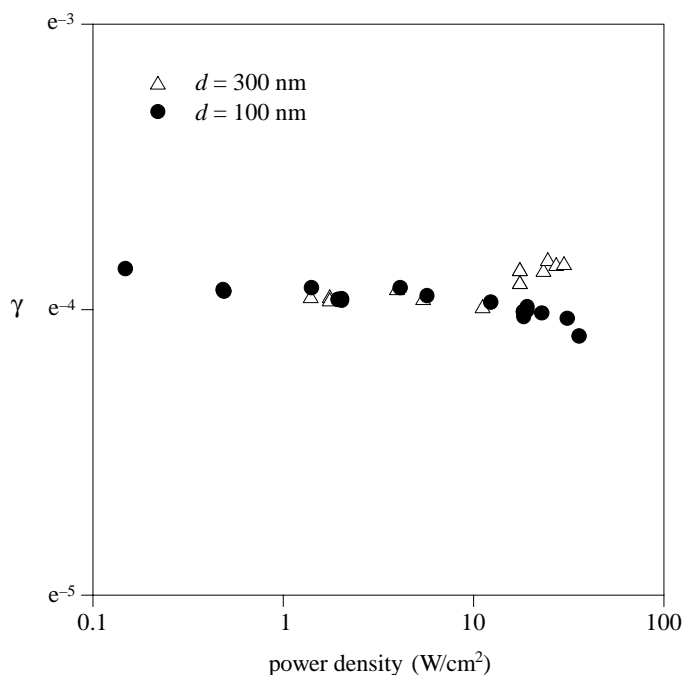
Figure 7. γ versus power density of the bleaching laser beam in the power density range of from 158 mW cm^{-2} to 55.2 W cm^{-2}.

different polymers, in terms of γ, differs by several orders of magnitude. Therefore, an error of 20% is relatively small if we want to compare the different polymers.

The fact that the determined quantum yield for bleaching is nearly independent of the bleaching power density over a wide range provides a fast method of determining the photochemical stability. If the γ was dependent on the bleaching power density it could not serve as a method to predict the lifetime of the polymer subjected to relatively low bleaching power densities, such as sunlight.

6. Wavelength dependency of γ

In the previous sections, the γ is determined for only one laser wavelength ($\lambda = 482$ nm). If γ is very dependent on the wavelength of the excitation source, a fair comparison of the stability with other polymers with a slightly different absorption spectrum would be impossible.

In order to determine the bleaching wavelength dependency of γ, the OC_1C_{10}-PPV sample is bleached with three different laser wavelengths. Bleaching experiments were performed using wavelengths of 355, 482 and 568 nm, which corresponds to absorption in the high-energy region, the centre of the peak and the low-energy tail, respectively (see figure 8). For these three wavelengths the initial absorption coefficient and γ, determined from a fit to the measured data, are given in table 2. The quantum yield for bleaching, γ, is fitted, for the different laser wavelengths with their absorption coefficient, to the transmission curves.

From table 2 we conclude that the quantum yield for bleaching for OC_1C_{10}-PPV is independent of the laser wavelength. This can be explained by the fact that the
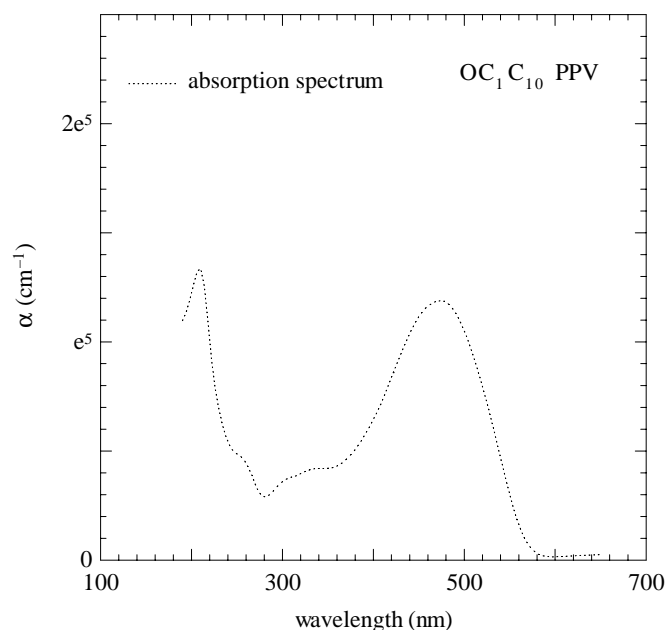
Figure 8. The absorption spectrum of OC_1C_{10}-PPV ($n = 0.12$).

Table 2. *The absorption coefficients and γ for different laser wavelengths*

	$\lambda = 355$ nm	$\lambda = 482$ nm	$\lambda = 568$ nm
α_0 (cm^{-1})	4.10×10^4	9.10×10^4	1.55×10^5
γ	1.50×10^{-4}	1.10×10^{-4}	1.20×10^{-4}

different excitation wavelengths are all situated in the same absorption peak in the case of OC_1C_{10}-PPV. The vibrational relaxation to the state with lowest vibrational energy is a very fast process, which makes it difficult for another process, such as degradation, to compete with.

7. O_2 concentration dependency of γ

The measurements presented in the previous sections were performed in air. It is well known that most photochemical degradation reactions are influenced by the presence of oxygen (Cumpston & Jensen 1995; Cumpston *et al.* 1997; Scott *et al.* 1996; Scurlock *et al.* 1995). We therefore investigated the influence of the oxygen concentration on γ. We performed a series of measurements at well-defined oxygen pressures. The polymer sample is placed in a vacuum chamber, which is pumped to a pressure below 5×10^{-6} mbar and filled with pure oxygen up to a certain pressure. The γ has been determined for oxygen pressures between 0.4 and 2500 mbar. Figure 9 shows the γ of OC_1C_{10}-PPV versus the oxygen pressure. The thickness of the polymer film is 360 nm and the laser wavelength is 482 nm.

The γ at an oxygen pressure of 200 mbar is approximately 1×10^{-4}, which is

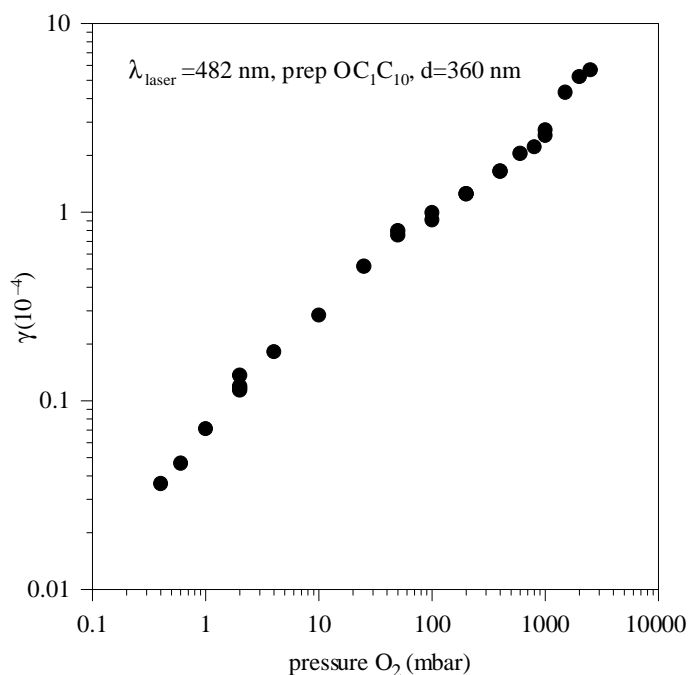Figure 9. γ of OC_1C_{10}-PPV versus the oxygen pressure. The thickness of the polymer film is 360 nm and the laser wavelength is 482 nm.

consistent with the γ at atmospheric air pressure (assuming 20% oxygen content of air). The γ was also measured in nitrogen, containing approximately 5 ppm oxygen (5×10^{-3} mbar partial oxygen pressure), resulting in a γ of 2.3×10^{-7}. The quantum yield for bleaching is not proportional to the oxygen pressure, but can be fitted by

$$\gamma = AP_{O_2}^{0.5},$$

where P_{O_2} is the oxygen pressure and A is a constant. An explanation may be found in the relation between the absorbed amount of O_2 molecules in the polymer layer and the O_2 pressure outside the polymer. The oxidation rate, and hence the stability of the polymer, will be more directly dependent on the concentration of the absorbed O_2 molecules in the polymer. The mechanism of the photochemical degradation was proposed by Cumpston (1995, 1997) and by Scurlock (1995). They proposed that singlet oxygen is the reactive species in the oxidation. Singlet oxygen is formed by energy transfer form the triplet excited state of the dialkoxy-PPV.

8. Conclusion

We have derived a formula that allows a quantitative study of the photochemical degradation of PPV materials. This is of interest because it will allow us to predict the stability of these materials in polymer LEDs, in the absence of other external factors that cause device degradation and failure. These electroluminescent devices operate by a similar mechanism to the photoluminescence mechanisms presented in this study. The polymeric materials used in these devices will therefore undergo similar chemical processes, in the absence and in the presence of oxygen.

As a quantitative measure for the photochemical degradation, a quantum yield for photodegradation is proposed, γ, being the inverse of the average number of photons a molecule can absorb before being destroyed. The experimentally observed changes in transmission of the PPV films are fitted with a formula that contains γ as the only adjustable variable.

The experiments show that γ is independent of the optical power of the light source used in the bleaching experiments, and independent of the wavelength, as long as this wavelength falls within the absorption spectrum of the PPV material.

In the presence of oxygen, the main degradation pathway is by photo-oxidation of the PPV material. This was observed earlier by others as well (Cumpston & Jensen 1995; Cumpston *et al.* 1997; Scott *et al.* 1996; Scurlock *et al.* 1995). Consequently, there is a strong dependence of γ on the oxygen concentration.

In the future, we will investigate other PPV derivatives, e.g. soluble dialkyl-PPV (Staring *et al.* 1994) and cyano-substituted PPV (Staring *et al.* 1995), as well as conjugated polymers that do not contain the reactive vinyl-linkage, e.g. PPP. This will allow us to study the relation between γ and both electronic and structural variations in the electro- and photoluminescent polymer materials.

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Discussion

B. Holmes (*Melville Laboratory, Cambridge, UK*). Does Dr Staring think the crosslinking and defects in OC_1–C_{10} and related polymers arises through a carbenoid intermediate?

E. G. J. Staring. We assume that the polymerization and crosslinking reactions proceed through carbenoid intermediates. However, we have not studied the mechanism in detail, and we have no hard evidence. I know that other mechanisms have been proposed.

E. A. Chandross (*Bell Laboratories, Lucent Technologies, USA*). Please comment on the influence of annealing the polymer for improving device performance.

E. G. J. Staring. We see no beneficial effect on polymer light-emitting diode operation after annealing the polymer film. We do see a redshift of the emission wavelength, which is indicative of a morphological change in the film.

A. Vecht (*School of Chemical and Life Sciences, University of Greenwich, UK*). Could Dr Staring give any further information on the following? (1) The performance of the light-emitting polymers under pulsed excitation. Clearly, this information is essential before large information context displays can be considered. (2) He described the photochemical degradation of the materials studied. Has he carried out any investigations of photodegradation in actual devices under operating conditions?

E. G. J. Staring. (1) We have only just started operating polymer light-emitting diodes under pulsed conditions. Clearly this is crucial for pixelated device application. It is too early to comment on the results. (2) We have not investigated photochemical degradation in actual polymer light-emitting diodes.

S. Moratti (*Cambridge University, UK*). Has Dr Staring looked at where on the polymer photo-oxidation accurs?

E. G. J. Staring. Infrared spectroscopy of the bleached samples of the dialkoxy-PPV samples we have studied, indicate that the main site of attack is at the vinylic group of the polymer mainchain.

F. Garnier (*Laboratoire Matériaux Moléculaires, Thiais, France*). Once a polymer has been degraded, after 10 000 h LED operation; did Dr Staring analyse any modifications concerning the morphology of the polymer?

E. G. J. Staring. During operation, when the sample is heated by Joule-heating, morphological changes take place in the polymer film. This is observed as a redshift of the emission wavelength. We do not think that this is the main reason for device degradation and failure. We think that the stability of the polymer material is not the limiting factor in the lifetime of the devices.