Donor-acceptor block copolymers
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Abstract
Singlet oxygen quantum yield ($\Phi_\Delta$) measurements were performed on the block copolymer DEH-PPV-$b$-P(MA-$stat$-C$_{60}$MS), incorporating both electron donating and electron accepting properties. As a comparison the $\Phi_\Delta$ was also measured for both active components (DEH-PPV and C$_{60}$). The transient triplet absorbance spectra for these three compounds were recorded in order to get a better understanding of the species responsible for the singlet oxygen production and therefore the oxidation of the DEH-PPV.
6.1 Introduction

One of the main concerns since the discovery of the electroluminescent properties of conjugated polymers has been their relative instability, limiting the lifetime of devices such as LEDs and PVDs. One of the primary degradation mechanisms is photo-oxidation, making encapsulation of devices necessary. It was found that conjugated polymers in presence of light and oxygen undergo scission of the vinyl double bonds under the formation of carbonyl groups. Later it was demonstrated by FTIR and UV–vis absorbance studies that in photovoltaic devices containing C₆₀, this photodegradation mechanism is inhibited. The photocurrent, however, still decreases in the presence of both oxygen and light and it is therefore of vital importance to get a better understanding of the influence of C₆₀ on the degradation mechanisms involved in photodegradation.

6.1.1 Photodegradation mechanism of conjugated polymers

The most likely mechanism for the photo-oxidation of π-conjugated polymers involves reaction of singlet oxygen with the vinyl bonds present in these polymer chains. The highly reactive singlet oxygen undergoes 1,2-cycloaddition across the vinyl double bond, after which the product either produces a biradical that reacts with the alkyl side-chains or, as most often found, cleaves to form two aldehydes.

The reactive singlet oxygen ($O_2 (\overset{1}{\Delta_g})$) is created from oxygen in the triplet ground state ($O_2 (\overset{3}{\Sigma_g}^-)$) following the mechanism (also depicted in the simplified Jablonski diagram in scheme 6.1):

\[
\text{Pol} + h\nu \Rightarrow \text{Pol}^* (S_n)
\]

\[
\text{Pol}^* (S_n) \Rightarrow \text{Pol}^* (S_1)
\]

\[
\text{Pol}^* (S_1) \Rightarrow \text{Pol}^* (T_1)
\]

\[
\text{Pol}^* (T_1) + O_2 (\overset{3}{\Sigma_g}^-) \Rightarrow \text{Pol} + O_2^* (\overset{1}{\Delta_g})
\]

Upon illumination of the polymer, an electron is promoted to a singlet excited state ($S_n$) and will vibrationally relax (internal conversion) to the first excited state ($S_1$). This electron can then either fall back to the ground state ($S_0$) radiatively (fluorescence) or non-
radiatively or undergo intersystem crossing (ISC) to the triplet state \( (T_1) \).\textsuperscript{15-17} This triplet excited state is long-lived (ca. 20-200 µs)\textsuperscript{18} and the electron can again return to the ground state (phosphorescence) or, if the triplet energy is high enough, energy transfer can take place to another substance, such as oxygen, which will promote an electron from the triplet ground-state to the singlet excited state. The creation of singlet oxygen by energy transfer from the polymer chain to triplet oxygen is thus a form of auto-destruction.

It was found by pulse radiolysis measurements that, when using a sensitizer, a polymer chain can accept several triplet excitations before they become saturated.\textsuperscript{17, 18} When these triplets encounter each other, triplet–triplet annihilation takes place under the emission of delayed fluorescence.\textsuperscript{19}

Electron transfer can compete with the energy transfer to oxygen and it was therefore proposed by Sarkas \textit{et al.} \textsuperscript{5} that this is the origin of the stabilizing effect of \( C_{60} \). Since electron transfer from conjugated polymers to \( C_{60} \) is very fast (on the order of 40 fs),\textsuperscript{20} it could compete with the formation of singlet oxygen and thereby reduce the rate of photo-oxidation. To study this effect more closely it would be necessary to measure the amount of singlet oxygen that is created upon illumination.

\textbf{Scheme 6.1} Simplified Jablonski\textsuperscript{14} diagram showing the energy levels of singlet and triplet states. \textit{a}) excitation, \textit{b}) vibrational relaxation, \textit{c}) fluorescence, \textit{d}) intersystem crossing, \textit{e}) phosphorescence, \textit{f}) energy transfer and \textit{g}) singlet oxygen phosphorescence.
6.1.2 Laser Flash Photolysis

One of the ways to measure the amount of singlet oxygen produced by a certain substance is by directly detecting the phosphorescence of singlet oxygen (at 1270 nm) following the excitation of aerated solutions. In laser flash photolysis measurements the excitation takes place with laser pulses and the luminescence intensity at 1270 nm as a function of laser intensity gives the singlet oxygen quantum yield ($\Phi_{\Delta g}$). When comparing to a standard with known quantum yield a good estimate for singlet oxygen quantum yields can be given.\textsuperscript{21} In figure 6.1.A the experimental setup for these measurements is depicted schematically.

Both the singlet oxygen quantum yield and the radiative decay rate constant ($k_r$) depend strongly on the type of solvent used.\textsuperscript{22} If different excited species are involved it could also depend on other factors such as the wavelength of excitation, although the laser

![Figure 6.1](image)
is usually only capable of producing light of specific wavelengths, depending on the harmonics of the laser.

Several studies indicate that C\textsubscript{60} is a great source of O\textsubscript{2} (\textsuperscript{1}Δ\textsubscript{g}),\textsuperscript{23, 24} with quantum yields that reach near unity, but in itself C\textsubscript{60} is very stable towards oxidation.\textsuperscript{25, 26} It is even used as an effective photosensitizer,\textsuperscript{27} which contradicts the suggestion of Sarkas \textit{et al.}\textsuperscript{5} that the reason for the stabilizing effect of C\textsubscript{60} lies in electron transfer to the fullerene. Concentrations for the flash photolysis experiments, however, are normally way too low for charge transfer to take place. It is therefore necessary to use a substance that has both donor and acceptor chemically linked to each other. Upon single substitution of the C\textsubscript{60}, such as the iminofullerene synthesized in chapter 4 via an azide intermediate, the photophysical properties change only slightly.\textsuperscript{28} If one would further substitute the fullerene, the photophysical properties could change quite dramatically.\textsuperscript{29}

### 6.1.2.2 Transient absorbance spectra of triplet excited states

To get a better understanding of the excited species involved in the degradation process, triplet state absorbance spectra of the different compounds can be compared. Several groups have already reported the transient absorbance spectra for the triplet states of C\textsubscript{60},\textsuperscript{23, 24} and different types of PPV oligomers (OPVs)\textsuperscript{30} and PPV,\textsuperscript{31} but to this day no compounds were measured incorporating both of these substances.

The setup used for the transient absorbance measurements (figure 6.1.B) is similar to the setup for the singlet oxygen yield measurements. After illumination of the sample by a laser flash, the absorbance of the solution sample at a certain wavelength is taken as a function of time. Transient (triplet) absorbance spectra can be obtained in such way by combining the data points at the same time after the laser pulse and at many different wavelengths.

### 6.2 Results and discussion

Flash photolysis studies were done for the semiconducting block copolymer DEH-PPV\textsubscript{3.9k}-b-P(MA-stat-C\textsubscript{60}MS)\textsubscript{8.0k}(21:1) (figure 6.2) and for the two photoactive components it consists of, namely C\textsubscript{60} and DEH-PPV. The PPV part of the block copolymer has an average molecular weight of 3.9 kg·mol\textsuperscript{-1} and the coil block has an average \textit{M}_n of 8.0 kg·mol\textsuperscript{-1} of which 25% is composed of C\textsubscript{60}. Figure 6.3 shows the absorbance spectra for these three compounds in benzene, which are normalized for the concentration (in µg/ml).
Figure 6.2  The chemical structure of \( \text{DEH-PPV}_{3.9k} - b - \text{P(MA-stat-C}_{60}\text{MS})_{8.0k}[21:1] \). 

Figure 6.3  The weight normalized UV-vis absorbance spectra of \( C_{60} \) (· · · · ·), \( \text{DEH-PPV}_{3.9k} \) (---) and \( \text{DEH-PPV}_{3.9k} - b - \text{P(MA-stat-C}_{60}\text{MS})_{8.0k}[21:1] \) (——).

\( C_{60} \) and DEH-PPV have a \( \lambda_{\text{max}} \) of 335 and 481 nm, respectively, and the block copolymer absorbance spectrum shows a combination of both these spectra. It is clear from these spectra that with excitation at 335 nm, both compounds will absorb and thus be excited. When an excitation wavelength closer to the absorbance maximum of the PPV is chosen, however, the absorbance of the fullerene is too low to give a reasonable amount
of excited species. It is therefore interesting to look at the results obtained at both 335 and 481 nm. The laser used in these experiments, however, is capable of only delivering certain wavelengths of light and therefore measurements were performed at 335 and 532 nm.

6.2.1 $O_2 (^1Δ_g)$ yield measurements

The singlet oxygen yields were measured in benzene for DEH-PPV and C$_{60}$ and of a block copolymer containing both substances with excitation at 355 nm. No comparison was done with blends, since the concentrations used for the measurements, on the order of several µg per ml, are too low for any interaction to take place between the compounds on the timescale of the measurements (µs). To rule out any solvent effect, all samples were measured in benzene and the concentration used was such that the absorbance ($A$) of the samples was around 0.4.

![Figure 6.4](image)

**Figure 6.4** The singlet oxygen phosphorescence decay curves for pristine C$_{60}$ obtained with different laser pulse intensities ($E$) with excitation at 355 nm.

Figure 6.4 shows an example of the singlet oxygen phosphorescence decay curves obtained via flash photolysis measurements with different laser pulse intensities ($E$), ranging from 0.15 to 0.81 mJ. Only the results for pristine C$_{60}$ are shown, since they give
the strongest response. The other compounds gave similar decay curves, but with lower intensities. The amount of singlet oxygen present in a solution is taken as the initial O₂ (1Δg) phosphorescence intensity at 1270 nm (I₀) at t₀, directly after the laser pulse. This value is extrapolated from the first order decay profiles and depends linearly on E. If the laser intensity is too high, however, saturation takes place and the experimental values will start to deviate from linearity.

To study the influence of the C₆₀ in the block copolymer, measurements were also performed at 532 nm, since C₆₀ does practically not absorb in this region as compared to the PPV. Normally if the same species is involved at both wavelengths, the value for Φₐ should be equal. In the case of PPV these values could differ slightly due to the polydispersity of the polymer, even if the samples have a polydispersity as low as 1.1. As stated in chapter 1, the absorbance maximum depends strongly on the length of the polymer and therefore the polymers absorbing around 532 nm could be significantly longer than the ones absorbing at 355 nm.

In all cases the relaxation time constant (k) was around 30 µs and the results can therefore be easily compared. Figure 6.5 and 6.6 show the results for the I₀ measurements as a function of laser intensity (E) at 355 nm and 532 nm, respectively. As can be seen in the inset in the top graph in figure 6.6, in some cases at high laser intensities saturation takes place and the I₀-values start to deviate from linearity (only shown for this case). In such cases only the values at lower intensities (solid points), where a linear response is found, were taken into account.

The value of Φₐ can be obtained from comparison of the slope of the E-I₀ plots (figure 6.5 and 6.6) to a standard with known Φₐ, after correction for the absorbance at the chosen wavelength. The standard used at 355 nm. is 1H-phenalen-1-one, which has a Φₐ of 0.93 in benzene,³² and the one used at 532 nm. is 5,10,15,20-tetraphenylporphine (TPP), with Φₐ = 0.89.³³ In order for the different measurements to be comparable, the absorbance intensities should also be of the same order, an absorbance (A) of 0.4 was chosen. If the absorbance is too high, the E-I₀ graph will deviate from linearity.
Figure 6.5  $E$ versus $I_0$ with excitation at 355 nm and their linear fits for $C_60$ (■), DEH-PPV$_{3.9k}$ (●) and DEH-PPV$_{3.9k}$-b-P(MA-stat-C$_{60}$MS)$_{8.0k}$[21:1] (▲). Inset: all data obtained for DEH-PPV, including data excluded from $\Phi_\Delta$ determination (○).

Figure 6.6  $E$ versus $I_0$ with excitation at 532 nm and their linear fits for DEH-PPV$_{3.9k}$ (●) and DEH-PPV$_{3.9k}$-b-P(MA-stat-C$_{60}$MS)$_{8.0k}$[21:1] (▲).
The singlet oxygen quantum yield values ($\Phi_{\Delta}$) as calculated from the slope of the E-I₀ graphs in figure 6.5 and 6.6.

<table>
<thead>
<tr>
<th></th>
<th>$\Phi_{\Delta}$ (355 nm.)</th>
<th>$\Phi_{\Delta}$ (532 nm.)</th>
</tr>
</thead>
<tbody>
<tr>
<td>C₆₀</td>
<td>0.88</td>
<td>c</td>
</tr>
<tr>
<td>DEH-PPV₃.⁹k</td>
<td>0.03</td>
<td>0.03</td>
</tr>
<tr>
<td>DEH-PPV₃.⁹k-b-P(MA-stat-C₆₀MS)₈.⁰k[21:1]</td>
<td>0.47</td>
<td>0.13</td>
</tr>
</tbody>
</table>

a) using 1H-phenal-1-one ($\Phi_{\Delta} = 0.93$) as standard.32
b) using TPP ($\Phi_{\Delta} = 0.89$) as standard.33
c) assumed to be equal to the $\Phi_{\Delta}$ at 355 nm.

The singlet oxygen quantum yields for the different compounds are given in table 6.1. It is clear from these results that the conjugated polymer in itself only leads to the production of very small amounts of singlet oxygen. As expected the fullerene, on the other hand, has a very high $\Phi_{\Delta}$. When the samples are excited at 355 nm, the total $\Phi_{\Delta}$ for the block copolymer can be calculated, as the approximate sum of the quantum yields for the PPV and the C₆₀ parts, following Eq. (6-1).

$$\Phi_{\Delta, tot} = f_{Fu} \cdot \Phi_{\Delta,Fu} + f_{PPV} \cdot \Phi_{\Delta,PPV}$$

(6-1)

Where $f_{Fu}$ and $f_{PPV}$ are the fractions of the total quantum yield ($\Phi_{\Delta, tot}$) originating in the fullerene and the PPV part, respectively. These values can be derived from the absorbance spectra by comparison with the spectra for pristine C₆₀ and homopolymer PPV, thus calculating the relative absorbance ($A$) of the two different parts, given by Eq. (6-2);

$$A_{tot} = A_{Fu} + A_{PPV}$$

(6-2a)

$$A_{Fu} = f_{Fu} \cdot A_{tot} \quad \text{and} \quad A_{PPV} = f_{PPV} \cdot A_{tot}$$

(6-2b) and (6-2c)

At 355 nm the factors were calculated to be $f_{Fu} = 0.69$ and $f_{PPV} = 0.31$, which means that 69% of the absorbance originates in fullerene absorbance and the other 31% in the PPV absorbance. From Eq. (6-1) a $\Phi_{\Delta, tot} = 0.62$ could be calculated, which is on the same order of the experimental value (0.47). The difference could be an indication of the difference between the iminofullerene mono-adduct and pristine C₆₀.28, 29
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The results obtained with excitation at 532 nm, however, show a completely different picture. This time \( f_{Fu} \) and \( f_{PPV} \) are found to be 0.03 and 0.97, respectively. Thus, even if the \( \Phi_\Delta \)-value is corrected for the small absorbance of C\textsubscript{60} at this wavelength, assuming that the \( \Phi_\Delta,Fu \) is the same at both wavelengths,\textsuperscript{24} the quantum yield for the block copolymer is still much higher than could be calculated from the quantum yields of the different compounds. When directly calculating the total \( \Phi_\Delta \) from this equation, it would be a factor of 2-4 lower than the experimental value, where in the case of excitation at 355 nm a slightly higher value is calculated than experimentally found, instead. This difference indicates that in this block copolymer even in solution electron transfer from the conjugated polymer to the fullerene takes place. When the electron is transferred from the singlet excited PPV to the C\textsubscript{60}, which then easily undergoes ISC to a triplet state, extra singlet oxygen is produced.

6.2.2 Transient triplet absorbance spectra

All transient triplet absorbance spectra were taken with N\textsubscript{2}-saturated solutions in order to prevent triplet quenching by O\textsubscript{2} and a flow cell was used to reduce the effect of sample bleaching during the measurements. In figure 6.7 and 6.8 the transient triplet absorbance spectra are depicted for C\textsubscript{60}, DEH-PPV and the DEH-PPV-\( b \)-P(\textit{MA-stat}-C\textsubscript{60}MS) block copolymer in benzene, as taken from the data obtained 2 \textmu s. after the excitation pulse.

The top graph (figure 6.7) shows the spectra for excitation at 355 nm. The triplet excited state of fullerene shows the same spectral features as reported previously,\textsuperscript{23, 24} and has an absorbance maximum around 740-750 nm. Also the spectrum for triplet DEH-PPV, though much weaker, shows mainly the same features as reported for a similar PPV (poly[2-methoxy-5-(2’-ethylhexyloxy)-1,4-phenylenevinylene] or MEH-PPV),\textsuperscript{31} with an absorbance maximum around 820 nm and bleaching of the ground state absorbance around 500 nm, as can be seen more clearly in the spectra from data obtained 20 \textmu s after the laser pulse (see inset). The block copolymer shows overall the same features as the pristine C\textsubscript{60} with a small shoulder to higher wavelength due to the triplet absorbance of the PPV part. This indicates that the main triplet species is the fullerene excited state, which is in agreement with the results from the O\textsubscript{2} (\(^1\Delta_g\)) quantum yield measurements.
Figure 6.7 The transient triplet absorbance spectra 2 μs. after excitation at 355 nm for $C_{60}$ (■), DEH-PPV$3.9k$ (●) and DEH-PPV$3.9k$-b-P(MA-stat-C$_{60}$MS)$_{8.0k[21:1]}$ (▲). Inset: spectrum for DEH-PPV$3.9k$ 20 μs. after the laser pulse.

Figure 6.8 The transient triplet absorbance spectra 2 μs after excitation at 532 nm for DEH-PPV$3.9k$ (●) and DEH-PPV$3.9k$-b-P(MA-stat-C$_{60}$MS)$_{8.0k[21:1]}$ (▲).
In figure 6.8 the transient absorbance spectra for DEH-PPV and the block copolymer are shown for excitation at 532 nm. The spectrum for PPV is essentially the same as the one for excitation at 355 nm. Also the block copolymer spectrum is the same as for excitation at 355 nm, the main triplet species is triplet excited fullerene. As stated before, C$_{60}$ shows only very weak absorbance at 532 nm as compared to the PPV part and this result can therefore only be explained by an electron transfer from the PPV to C$_{60}$ and subsequent formation of triplet C$_{60}$.

6.3 Conclusions

The results of the singlet oxygen quantum yield measurements by flash photolysis with excitation at 355 nm. for C$_{60}$ ($\Phi_{\Delta} = 0.88$) confirmed the high quantum yield reported by Arbogast et al.$^{23}$ The DEH-PPV derivative showed a thirty-fold lower O$_2$ ({$^1\Delta_g$}) quantum yield and for the block copolymer DEH-PPV-$b$-P(MA-stat-C$_{60}$MS) $\Phi_{\Delta}$ (0.47) could be calculated as the absorbance related sum of the separate quantum yields of the PPV and C$_{60}$ part. The transient triplet absorbance spectra of the compounds showed the same behavior, where the spectrum for the block copolymer showed essentially the triplet state of C$_{60}$ with a small shoulder from the triplet PPV.

When the block copolymer is excited at 532 nm., both the $\Phi_{\Delta}$ and the transient absorbance spectrum indicate the large abundance of triplet C$_{60}$, as compared to what can be expected from the absorbance at this wavelength. This is an indication for electron or energy transfer from the PPV part to the fullerenes. This electron transfer competes with the formation of polymer in the triplet state, as proposed by Sarkas et al.$^5$. His conclusion, however, that the amount of singlet oxygen that is formed would be lower in that case is incorrect, the inverse is true. The singlet oxygen production is increased due to the energy transfer from (more abundant) triplet fullerene to triplet oxygen.

With the amount of singlet oxygen produced being raised, one would expect C$_{60}$ to have a negative influence on the stability of conjugated polymers. It is therefore not clear what is the origin of this stabilizing effect. It must be noted that this stabilizing effect was obtained in thin films,$^{5-7}$ where the slow diffusion of oxygen might play a major role. The presence of fullerene crystallites in such blend films could reduce the diffusion of gasses into the film limiting the degradation of conjugated polymers mixed with C$_{60}$. Theoretically, if the triplet state of the conjugated polymer is longer lived than the triplet excited state of fullerene, the triplet state would have a smaller diffusion range, decreasing the chance of energy transfer to oxygen. These solution measurements are only possible due to the fact that both components are present in the same macromolecule. In a normal
dilute solution of a mixture of the two the timeframe for the measurements would be too short to allow for charge or energy transfer between the two substances.

### 6.4 Experimental section

**Materials**

C\textsubscript{60} (99.5\% pure) was purchased at MER Corporation and stored in the dark. DEH-PPV ($DP_n \approx 10$) was synthesized as described in chapter 2 (47 hours at rt.) and purified via column chromatography. The block copolymer DEH-PPV-\textit{b}-P(MA-\textit{stat}-C\textsubscript{60}MS) was synthesized from a macro-initiator based on the PPV used in these experiments, as described in chapter 3 and 4. The respective molecular weights of the two blocks are $\sim 3.9$ and $\sim 8.0$ kg·mol$^{-1}$ (11.9 in total), where the second block contains approximately 25 wt-% of C\textsubscript{60} ($\sim 16$ wt-% of the total block). All samples were stored in the dark and the block copolymer was kept under Argon. All experiments were carried out in spectroscopic grade benzene.

**Measurements**

UV-vis spectra were measured in UV grade benzene with a Shimadzu UV-2101PC UV-VIS Scanning Spectrophotometer and corrected for the concentration in µg/ml.

Laser flash photolysis studies were made at the Free Radical Research Facility (FRRF) at the CCLRC Daresbury Laboratory (UK). Studies were performed with the a Q-switched JK Lasers System 2000 Laser with Nd-YAG oscillator and Nd-glass amplifier equipped with frequency doubling, tripling and quadrupling crystals. The second or third harmonic ($\lambda = 532$ or 355 nm) were used and a pulse length of 15 ns. (fwhm = 15 ns.). Data were collected using a Tektronix TDS380 digital oscilloscope with a maximum sampling rate of 2 GHz.

The sample solutions were made with concentrations corresponding to an absorbance of approximately 0.4 per cm optical path length at the respective wavelength. For the singlet oxygen quantum yield measurements these solutions were placed in a quartz cell with a 10 mm path length, irradiated with single pulses delivered by the laser with varying intensities (ranging from 0-6 mJ). The $O_2(1\Delta_g \rightarrow 3\Sigma_g^+)$ phosphorescence at 1270 nm was recorded using a cryogenic germanium diode (North Coast EO817P). As standards for the calculation of the singlet oxygen quantum yields $1H$-phenal-1-one (for excitation at 355 nm, $\Phi_\Delta = 0.93$)\textsuperscript{32} and TPP (for excitation at 532 nm, $\Phi_\Delta = 0.89$)\textsuperscript{33} were used. The values of $\Phi_\Delta$ were obtained from the slopes of the respective $E$-$I_0$ plots.
For the measurements of the transient triplet absorbance spectra, the samples were deoxygenated by means of saturation with N₂ (bubbling through for 15 min). A 10 mm quartz cell was replenished after each laser pulse, making use of a flow system. Samples were irradiated with single pulses of the following intensities: ~3.5 mJ for C₆₀, ~12 mJ at 355 and ~98 mJ at 532 nm for DEH-PPV, and ~9 and ~110 mJ for the block copolymer at 355 and 352, respectively. The transient absorbance was measured using a pulsed Xe arc lamp and spectra were compiled point-by-point.
6.5 References

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