



Photo-oxidation in an $^{18}\text{O}_2$ atmosphere: A powerful tool to elucidate the mechanism of UV–visible light oxidation of polymers – Application to the photodegradation of MDMO-PPV

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ABSTRACT

This article describes a new approach to improve the analysis of the chemical modifications that result from the degradation of polymers under UV–visible light exposure in the presence of oxygen. The tool which is used consists of an irradiation chamber whose atmosphere is composed of $^{18}\text{O}_2$. The $^{18}\text{O}_2$ pressure inside the chamber and the hygrometry can be adjusted. In this study, particular attention was paid to the photo-oxidation of poly[2-methoxy-5-(3',7'-dimethyloctyloxy)-1,4-phenylenevinylene] (MDMO-PPV). Using infrared spectroscopy, irradiation under the oxygen 18 atmosphere allowed discrimination between compounds formed via fixation of oxygen from the atmosphere and those formed by reorganisation of the matrix. In addition, irradiation of MDMO-PPV in an $^{18}\text{O}_2$ wet atmosphere allowed for detection of the presence of phenyl formate and aromatic ketone functions. This permitted validating the mechanism of photo-oxidation previously proposed. Additionally, with regard to blends made with MDMO-PPV and methano-fullerene[6,6]-phenyl C_{61} -butyric acid methyl ester ([60] PCBM), it was demonstrated that this technique facilitates the identification of the photo-oxidation products formed.

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1. Introduction

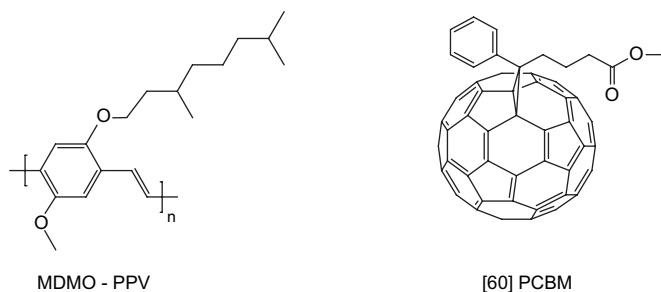
Exposure of polymers to UV–visible light or to moderate temperatures induces chemical modifications of their structure. These changes are likely to modify the macroscopic properties of the polymer and, as a consequence, are responsible for deterioration of the performance of the structure in which the material is used [1,2]. In order to understand the changes of the chemical structure, several tools exist that permit analyzing and understanding the mechanism of degradation including infrared (IR), UV–visible and fluorescence spectroscopies, Size Exclusion Chromatography (SEC), and Nuclear Magnetic Resonance (NMR). The most useful of these methods is most likely IR spectroscopy, which gives information on the modifications of the chemical structure that result from the ageing of the material, especially in the case of oxidative degradation. The formation of oxidation products usually leads to the appearance of new absorption bands in the carbonyl region (envelope observed in the range $1900\text{--}1500\text{ cm}^{-1}$) [3–5]. Chemical derivatisation methods can be used to simplify the spectrum of an

oxidised specimen, which is rather important when the bands overlap. This permits in turn the identification and quantification of the various absorbing species composing the IR spectrum of the oxidised materials [6,7]. This approach can be described as chemical deconvolution. However, it does not make a distinction between oxidation products formed by the fixation of atmospheric oxygen onto the macromolecular chains and rearrangements involving an oxygen atom that would be part of the chemical structure of the polymer. This is exemplified in the case of polyamides, polyethers, phenoxy resins or PMMA [8–11].

Oxygen 18 isotopic labelling is a widely used technique to study degradation processes by IR [12,13], TOF-SIMS [13–15] or LC–MS [16] analysis. In our case, we developed a tool that permits irradiations of polymers in the presence of $^{18}\text{O}_2$ at fixed pressure and hygrometry. Because the atomic mass of this oxygen isotope has a direct incidence on the IR frequency of the carbonyl products formed by the fixation of atmospheric oxygen; these products can be discriminated from those resulting from rearrangements of the polymeric matrix, as the macromolecular backbone of the polymer also contains oxygen atoms in its structure. This tool also provides the possibility to analyze the effect of the presence of water during photodegradation.

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Scheme 1. Chemical structure of MDMO-PPV and [60] PCBM.

We focused our attention on the photo-oxidation of pristine MDMO-PPV (poly[2-methoxy-5-(3',7'-dimethyloctyloxy)-1,4-phenylenevinylene]) and MDMO-PPV blended with [60] PCBM (methano-fullerene[6,6]-phenyl C₆₁-butyric acid methyl ester) (Scheme 1). The ageing of these components, which are used in the active layer of organic photovoltaic devices [17,18], has been recently studied by our group [19,20]. A mechanism of photo-oxidative degradation has been proposed to account for the ageing of MDMO-PPV [20].

2. Experimental

MDMO-PPV was supplied by Imec Laboratory (Belgium). The molecular weight of the polymer was determined by Size Exclusion Chromatography as 250,000 g mol⁻¹; the calibration was achieved using polystyrene standards. PCBM was provided by the University of Groningen.

Thin films of MDMO-PPV and MDMO-PPV:PCBM (1:4 ratio) were prepared in a glove box. Samples were cast from chlorobenzene (provided by Aldrich) solution on ITO-coated glasses or CaF₂ using spin-coating technique (G3P-8 Spincoat from Cookson Electronics Equipment). Spin-coating parameters were 1500 rpm for the velocity, 500 rpm s⁻¹ for the acceleration and 2 min for the duration. This permits homogeneous films of 140 nm to be

obtained for MDMO-PPV and 240 nm for MDMO-PPV:PCBM blends. The thickness of the samples was determined by profilometry using a DEKTAC apparatus. Before irradiation under ¹⁸O₂, the samples were kept in a glove box without light exposure.

In the case of photo-oxidation in ¹⁸O₂, irradiations were carried out using a halogen lamp (OSRAM). ¹⁸O₂ was obtained from Eurisotop with an isotopic purity of 97%. Photo-oxidations in ¹⁶O₂ were performed using a SEPAP 12/24 unit providing an artificial ageing corresponding to medium accelerated conditions [21]. This chamber is made of a square reactor equipped with four medium-pressure mercury lamps (Mazda MA 400) situated in vertical position at each corner of the chamber. In the centre of the chamber, the samples were fixed on a rotating carousel with a 13 cm diameter that could hold 24 samples. In this series of experiments, the temperature at the surface of the samples was fixed at 60 °C.

Water treatments consisted of immersing the samples after exposure in steam produced by boiling water.

Infrared Reflection-Absorption Spectroscopy (IRRAS) and transmission mode were used to study the chemical modifications of the samples. Spectra were recorded with a Nicolet 760-FTIR spectrophotometer working with OMNIC software (128 scan summations and 4 cm⁻¹ resolution).

2.1. Irradiation under dry ¹⁸O₂ atmosphere

Fig. 1 represents the system used for the preparation and irradiation of the samples under ¹⁸O₂.

In order to avoid the possible influence of atmospheric oxygen (¹⁶O₂) during irradiation, the samples were prepared under inert atmosphere (anhydrous nitrogen) in a glove box. The sample to be irradiated was transferred from the glove box to the irradiation chamber using a portable container under anhydrous nitrogen. The portable container was then connected to the irradiation chamber with an O-ring system.

Before filling the irradiation chamber with dry ¹⁸O₂, several steps have to be performed in order to adjust the composition of

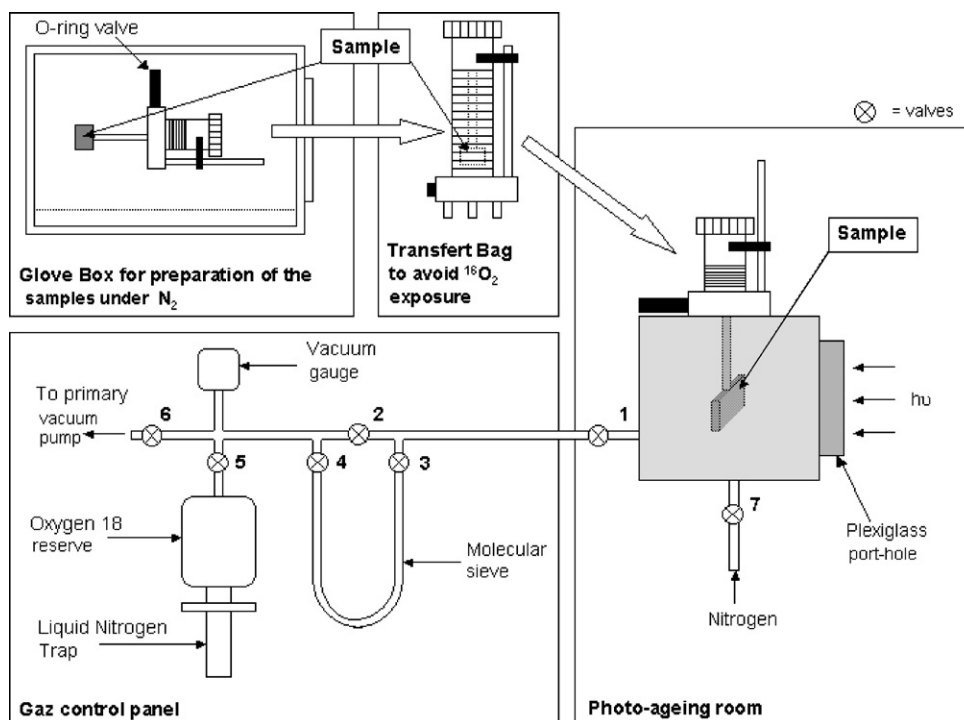


Fig. 1. Schematic drawing of preparation chamber and of irradiation system.

the atmosphere in the irradiation chamber (see Fig. 1). First, three cycles of evacuation (valves 1, 2 and 6 opened)/refilling with anhydrous N_2 (valve 1 closed and valve 7 opened) were done. Then, the O-ring valve of the portable container was opened, the sample was placed in the chamber and a last evacuation was done to eliminate nitrogen from the irradiation chamber. By closing valves 2, 6 and 7 and opening valves 1, 3–5, the chamber was filled with dry $^{18}O_2$ contained in the reserve, and then valve 1 was closed. The molecular sieve acted as a trap for residual water molecules.

During irradiation, the pressure in the chamber was monitored by a gauge and the temperature was controlled and maintained in the range of 25–30 °C.

After irradiation, dry $^{18}O_2$ was trapped back by cooling the reserve with liquid nitrogen and opening valves 1, 3–5. When the pressure reached a minimum value (100–200 Pa), valve 5 was closed and valves 2 and 6 were opened to remove the residual atmosphere inside the chamber. The O-ring valve of the portable container was then closed.

2.2. Irradiation under wet $^{18}O_2$ atmosphere

Depending on the hygrometry needed, a solution of saturated salt was prepared [22] (NaCl for 80% relative hygrometry, no salt for 100% relative hygrometry), frozen with liquid nitrogen and placed in the irradiation chamber. The procedure was the same as previously described except that a waiting period of several hours was used to stabilise hygrometry after opening the O-ring valve of the portable container but before irradiation. After irradiation, the recovery procedure of atmosphere was the same as previous and the molecular sieve permitted the recovery of dry $^{18}O_2$. Finally, the residual atmosphere in the irradiation chamber was pumped with the primary vacuum pump and the portable container was closed.

3. Results and discussion

Ageing under an oxygen 18 atmosphere was first applied to pristine MDMO-PPV. A number of doubts have been raised previously concerning the identification of the IR bands appearing during photo-oxidation, and this technique was expected to improve our understanding of the degradation. Two kinds of irradiation in the $^{18}O_2$ atmosphere were carried out: the first one under a dry atmosphere using only the atmosphere contained in the reserve; the second one under a wet atmosphere (100% humidity) using both the $^{18}O_2$ atmosphere contained in the reserve and water vapour from a bath of $H_2^{16}O$.

In the second part of this study, the method was applied to MDMO-PPV:PCBM blends. This technique should be very useful as the methyl ester IR band of the PCBM hides the formation of the photoproducts.

3.1. Pristine MDMO-PPV

3.1.1. Irradiation under dry conditions

MDMO-PPV samples of 140 nm spin-coated on glass:ITO substrates were irradiated in a dry oxygen 18 atmosphere. The chamber was filled with pure $^{18}O_2$ at a pressure of 20,600 Pa, which corresponded to the oxygen partial pressure in the atmosphere ($P_{O_2} = 101,330 \times 0.2 = 20,266$ Pa). The temperature inside the chamber was fixed at 27 °C. The sample was irradiated for 180 min. In parallel, MDMO-PPV samples prepared under the same conditions were irradiated in the SEPAP 12/24 unit. Irradiation was carried out in ambient air ($P_{O_2} = 20,266$ Pa; $P_{N_2} = 81,064$ Pa) and the temperature of the sample was maintained at 60 °C.

Fig. 2 shows the IR spectra in the carbonyl region for both samples before irradiation and after irradiation either in $^{18}O_2$ or in $^{16}O_2$.

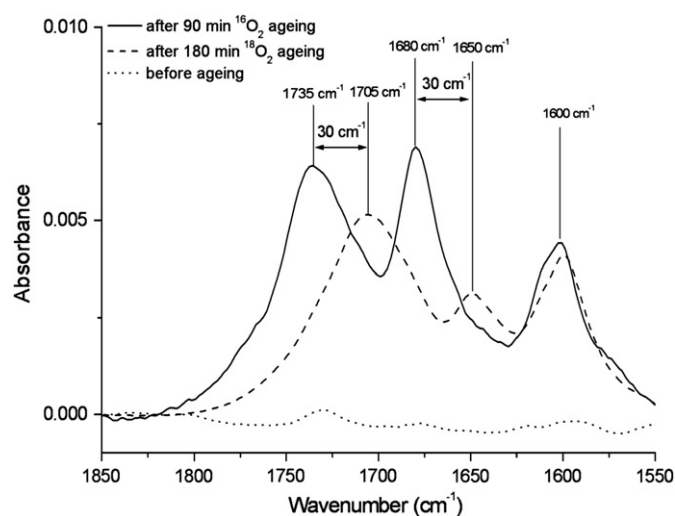


Fig. 2. IR spectra in the carbonyl region (1850–1550 cm^{-1}) of MDMO-PPV samples before ageing (dot line), irradiated in presence of $^{18}O_2$ (dash line) and irradiated in presence of $^{16}O_2$ (solid line).

In the case of the sample irradiated in $^{16}O_2$, one can observe in Fig. 2 three bands in the carbonyl region, centred, respectively, at 1735, 1680 and 1600 cm^{-1} . In a previous study, these bands were attributed to three different species: the band centred at 1735 cm^{-1} to a complex mixture of ester, formate and carboxylic acids, and the band centred at 1680 cm^{-1} to an aromatic ketone [20]. According to the degradation mechanism previously proposed, the carbonyl products (absorption at 1735 and 1680 cm^{-1}) are formed by fixation of oxygen involving a chain oxidation reaction. It was previously proposed that the band at 1600 cm^{-1} is characteristic of a ring vibration [23–25] and could result from a shift of frequency of the band present at 1591 cm^{-1} before irradiation, indicating changes of ring substitution. The shift of this band would be accompanied by an increase in intensity.

In the case of the sample aged under $^{18}O_2$, three bands in the carbonyl region were also detected, but for two of them the frequency was different, as the bands were centred, respectively, at 1705, 1650 and 1600 cm^{-1} . It may be anticipated that the observed shift of frequencies resulted from the changes of the reduced mass of the C=O oscillator. Calculations based on the classical equation between the frequency and the reduced mass suggest that a shift of around 35–40 cm^{-1} can be expected when passing from $^{16}O_2$ to $^{18}O_2$ [13]. Taking into account this value, the analysis of the IR spectra shown in Fig. 2 first suggests that the frequencies of products formed under conditions of irradiation in $^{16}O_2$ at 1735 and 1680 cm^{-1} , were, respectively, shifted to 1705 and 1650 cm^{-1} when irradiations were carried out under $^{18}O_2$. The slight difference between the experimental and the theoretical shift can be explained by the surroundings of the carbon atom. In fact, as the carbon atom carrying the carbonyl group is not isolated but attached to adjacent carbon atoms, the frequency will change somewhat. These results strongly suggest that the photoproducts at 1735 and 1680 cm^{-1} result from an oxidation of the polymeric matrix by fixation of oxygen from the atmosphere, following the mechanism previously reported [20].

Fig. 2 shows that the band at 1600 cm^{-1} was not shifted when irradiation was carried out under $^{18}O_2$ or $^{16}O_2$. This result confirms that this band does not correspond to a carbonyl product issue from the fixation of atmospheric oxygen, but is the characteristic of the polymer, whose intensity and frequency are modified with the substitution of the ring.

Fig. 3 shows with more detail how the IR spectrum in the carbonyl region of MDMO-PPV sample was modified with increasing

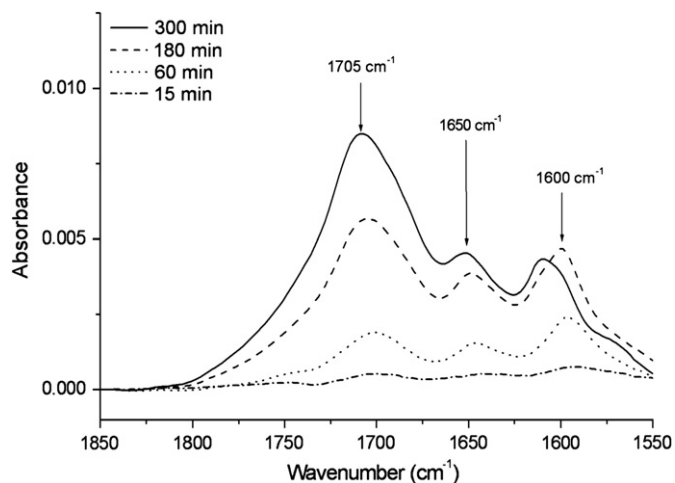


Fig. 3. IR spectra changes of MDMO-PPV caused by UV-light irradiation ($\lambda > 300$ nm) under $^{18}\text{O}_2$. Subtraction spectra: 300–0 min (solid line); 180–0 min (dash line); 60–0 min (dot line) and 15–0 min (dash dot line).

irradiation times in the presence of $^{18}\text{O}_2$, starting from 15 min of exposure to 300 min.

Concerning the bands resulting from the formation of photo-products by fixation of oxygen, only the ones at 1705 and 1650 cm^{-1} could be observed. No oxidation products resulting from reaction with $^{16}\text{O}_2$ could be detected. This result indicates that the sample was not contaminated by oxygen from the atmosphere ($^{16}\text{O}_2$) during the preparation or the analysis process and that the quantity of oxygen that could be trapped in the polymer was not sufficient to induce a significant and detectable degradation. This result validates the procedure. The irradiation chamber and the portable container were verified as being very tight.

3.1.2. Irradiation under wet conditions

Under $^{18}\text{O}_2$. MDMO-PPV was irradiated in an $^{18}\text{O}_2$ atmosphere with 100% humidity. The pressure inside the chamber was about 21,600 Pa and the temperature was 30 °C. Fig. 4 shows the spectrum of the sample after 3 h of exposure. The IR spectrum of a sample irradiated under dry conditions is plotted in the same figure.

It can be observed in Fig. 4 that on one hand wet irradiation provoked the formation of a carbonyl band centred at 1680 cm^{-1} , and on the other hand that the concentration of the photoproducts

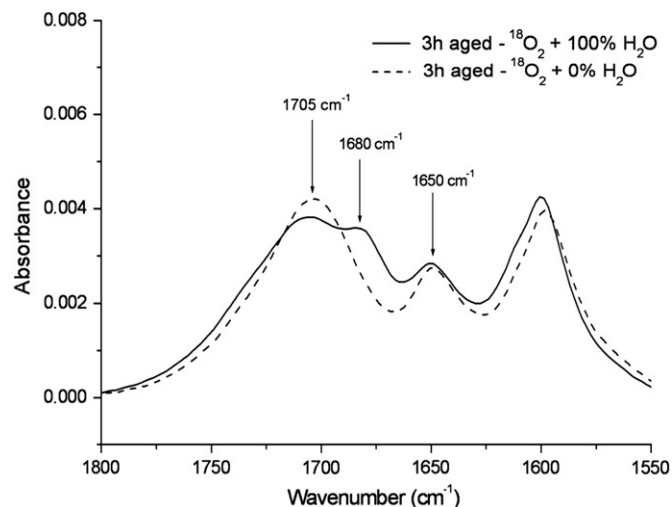


Fig. 4. IR spectra in the carbonyl region (1850–1550 cm^{-1}) of MDMO-PPV irradiated in $^{18}\text{O}_2$ and 0% H_2O (dot line), and in $^{18}\text{O}_2$ and 100% H_2^{16}O (solid line).

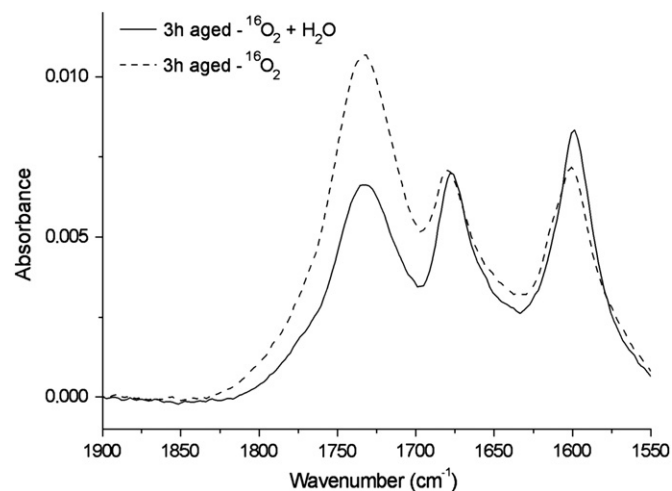


Fig. 5. IR spectra in the carbonyl region (1850–1550 cm^{-1}) of MDMO-PPV irradiated in $^{16}\text{O}_2$ and 0% H_2O (dot line) and in $^{16}\text{O}_2$ and 100% H_2^{16}O (solid line).

formed at 1705 cm^{-1} was smaller under the wet atmosphere than under the dry atmosphere. These results suggest that water modified the photodegradation process, probably by reacting with the photoproducts. Two experiments were carried out to validate this hypothesis: wet irradiation in $^{16}\text{O}_2$ with 100% humidity and dry irradiation in $^{18}\text{O}_2$ followed by an exposure to water vapour.

Under $^{16}\text{O}_2$. The IR spectra in the carbonyl region of MDMO-PPV irradiated for 3 h in a dry $^{16}\text{O}_2$ atmosphere and in a wet $^{16}\text{O}_2$ atmosphere are compared in Fig. 5.

The spectra shown in Fig. 5 indicate that the ratio between the concentrations of the products absorbing, respectively, at 1735 cm^{-1} and at 1680 cm^{-1} was influenced by the presence of water during exposure. The amount of photoproducts absorbing at 1735 cm^{-1} was more important in the case of the dry irradiation. As reported above, this result could indicate a hydrolysis of the photoproducts during the wet irradiation. However, in contrast to the results given above for the wet irradiation in $^{18}\text{O}_2$, the decrease of the intensity of the

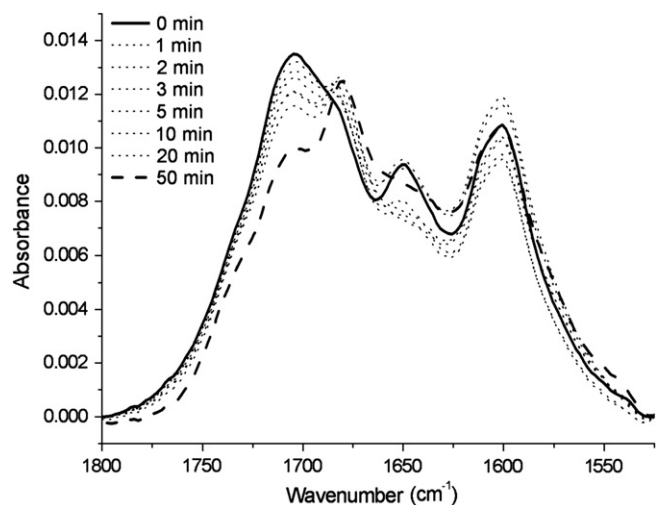
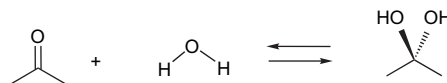
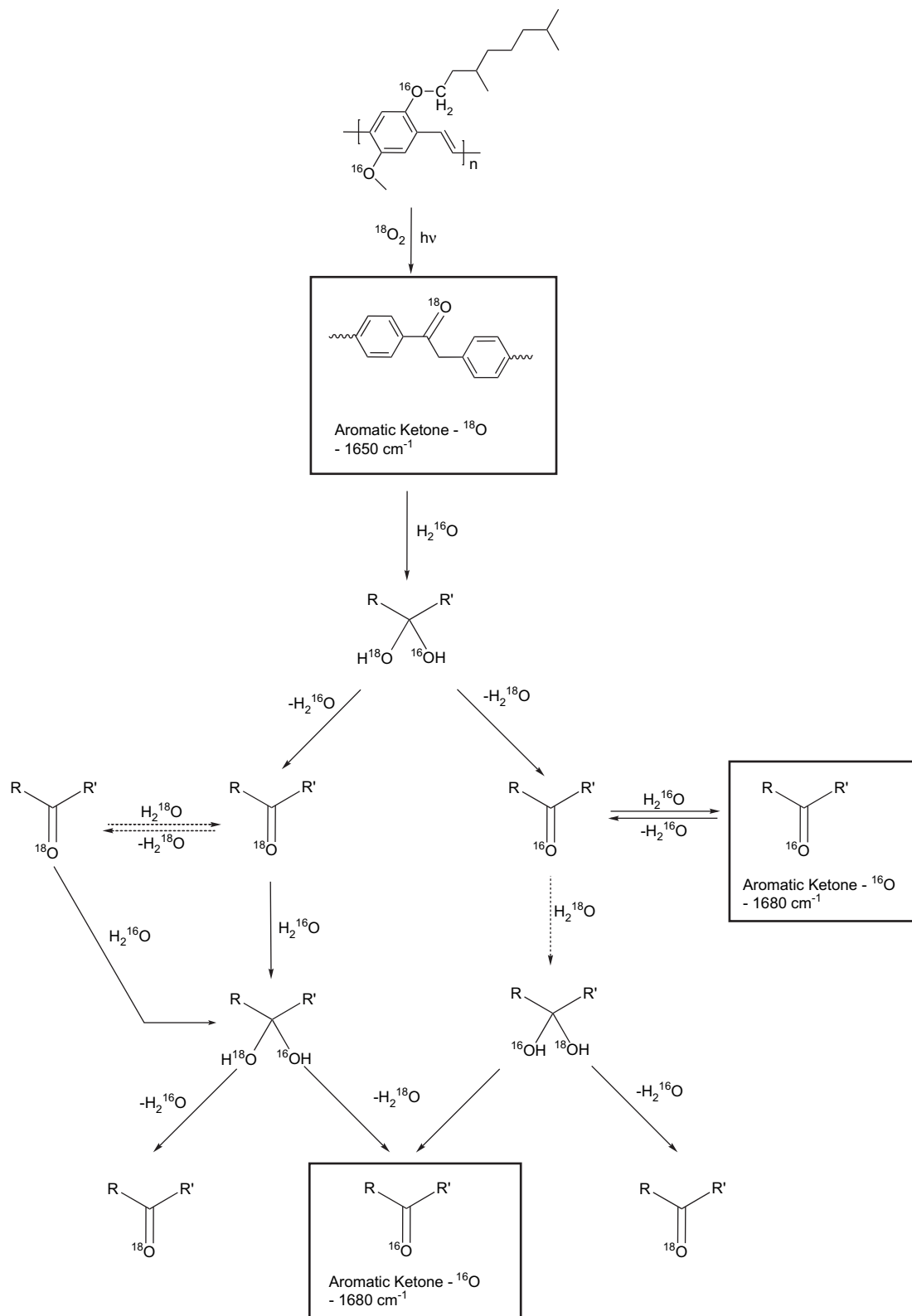


Fig. 6. IR spectra in the carbonyl region (1850–1550 cm^{-1}) of 3 h aged MDMO-PPV sample during exposure to water vapour.



Scheme 2. Equilibrium between ketone and gem-diol compounds in the presence of water.



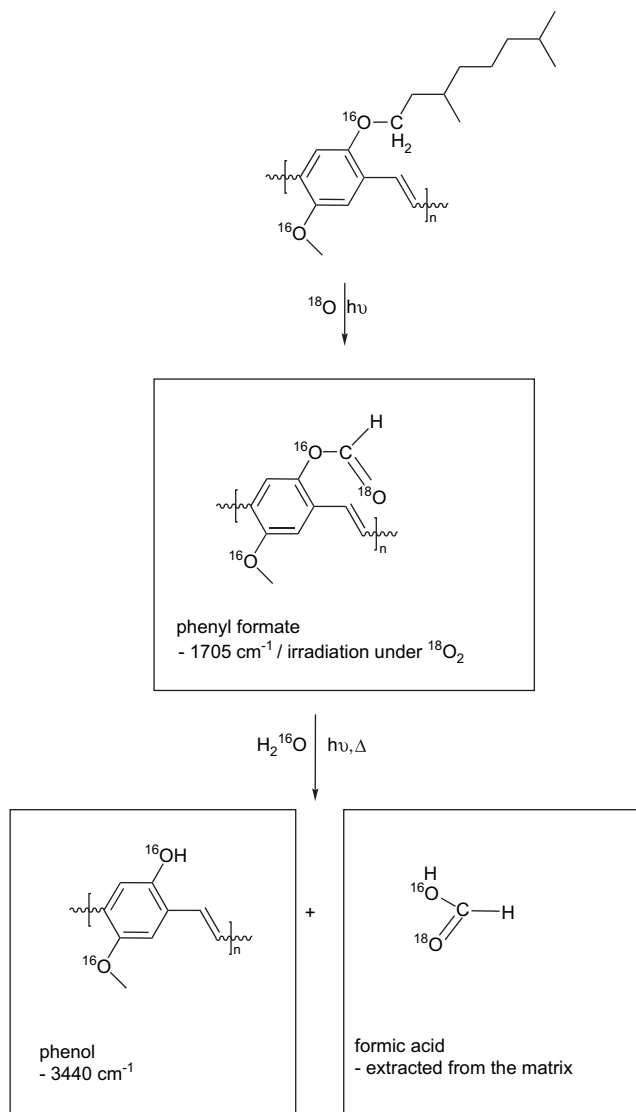
Scheme 3. Exchange of the oxygen 18 atom of the ketone with the oxygen 16 of water (H_2^{16}O).

band at 1735 cm^{-1} was not accompanied by the formation of a new band. It can therefore be concluded that the hydrolysis of the photoproduct did not generate a compound absorbing at 1680 cm^{-1} .

It is recalled that the carbonyl band that develops at 1735 cm^{-1} under $^{16}\text{O}_2$ irradiation (1705 cm^{-1} under $^{18}\text{O}_2$) corresponds to a complex mixture of products. One of them was identified as

phenyl formate. Such moieties are well known to undergo hydrolysis giving molecular formic acid [26].

Exposure to water vapour after $^{18}\text{O}_2$ irradiation. MDMO-PPV was first irradiated in $^{18}\text{O}_2$ for 180 min and then exposed to water vapour for times ranging from 0 to 50 min. Fig. 6 shows the resulting modifications in the carbonyl domain.



Scheme 4. Reactions of formation and hydrolysis of phenyl formate.

Fig. 6 shows two major events: first, the photoproduct absorbing at 1650 cm^{-1} disappeared after 50 min of exposure to water vapour and second a product was formed in parallel with an absorption at 1680 cm^{-1} . Both absorption bands in fact correspond to a unique product, which is an aromatic ketone with a carbonyl that contains either an oxygen 16 atom (1680 cm^{-1}) [20] or an oxygen 18 atom (1650 cm^{-1}). The shift observed during exposure to water suggests that the initial oxygen 18 atom of the aromatic ketone was exchanged with an oxygen 16 atom from the water. This reflects the equilibrium between the ketone and a *gem*-diol in the presence of water (Scheme 2) [27].

In the presence of water, the ketone (with an oxygen 18 atom) was transformed into a *gem*-diol compound, with two alcoholic functions: one with an oxygen 16 atom and the other with an oxygen 18 atom. The *gem*-diol can be transformed again into a ketone but, through this alternate pathway, the ketone can be formed with an oxygen 16 atom and water with an oxygen 18 atom. The different steps that can occur during this exchange are summarized in Scheme 3.

The second event resulting from the water treatment observed in Fig. 6 was a decrease in the intensity of the band at 1735 cm^{-1} , which corroborates the behaviour observed during the wet irradiation experiments (see Fig. 4). The wet irradiation in $^{16}\text{O}_2$ indicates

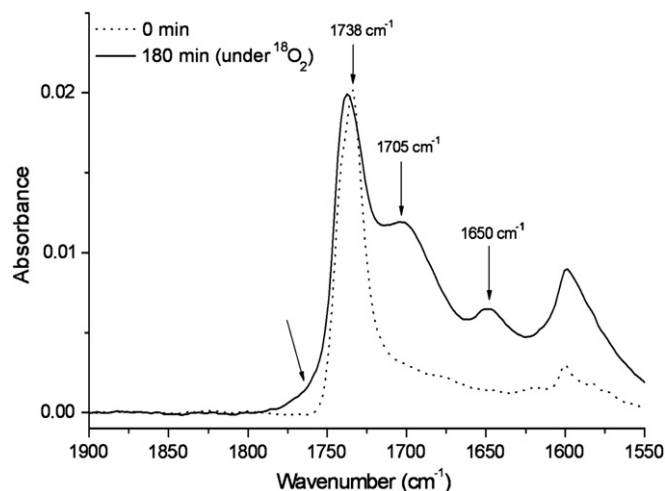


Fig. 7. IR spectra of MDMO-PPV:PCBM before (dot line) and after (solid line) 180 min of UV-light irradiation ($\lambda > 300 \text{ nm}$) under $^{18}\text{O}_2$.

that no other product was formed at the expense of this photoproduct. This result confirms that the reacting species were formates. The hydrolysis of these species led to the formation of formic acid that could be extracted from the polymer matrix. The reactions of the formation of phenyl formate by photo-oxidation and subsequent hydrolysis into formic acid in the presence of water are summarized in Scheme 4.

3.2. MDMO-PPV:PCBM blend

The methodology was then applied to MDMO-PPV blended with PCBM. The IR band of the methyl ester group of PCBM hides the formation of oxidation products, making it difficult to identify the appearing species.

Samples of MDMO-PPV blended with PCBM were submitted to 180 min of irradiation under a dry oxygen 18 rich atmosphere ($P_{\text{O}_2} = 101,330 \times 0.2 = 20,266 \text{ Pa}$, $T = 27^\circ\text{C}$). Fig. 7 shows the IR spectra between 1900 and 1550 cm^{-1} of the sample before and after irradiation.

One can observe in Fig. 7 that the IR bands corresponding to the photoproducts were clearly separated from the initial methyl ester IR band. Two maxima were detected, the first one at 1705 cm^{-1} and the second one at 1650 cm^{-1} . Their frequencies correspond to those of the photoproducts of pristine MDMO-PPV. These results suggest that the mechanism of degradation of the polymer is identical in both the pristine and the blended films.

Moreover, a broadening of the initial carbonyl IR band centred at 1738 cm^{-1} could be observed with a shift towards higher frequencies. This result suggests that a photoproduct appeared that overlapped with the methyl-ester band. In a previous study, we showed that a photoproduct characteristic of the oxidation of C_{60} moieties appeared at 1782 cm^{-1} for irradiations in $^{16}\text{O}_2$ [19]. In an $^{18}\text{O}_2$ atmosphere, the absorption band of this product was shifted and convoluted with the methyl-ester band. This clearly indicates that this photoproduct was formed via fixation of oxygen.

4. Conclusion

The technique that consists of irradiating polymers in $^{18}\text{O}_2$ brings very valuable information that strongly facilitates the elucidation of oxidation mechanisms.

In the case of MDMO-PPV, this technique was decisive for the elucidation of the oxidation mechanism. It has now been demonstrated that all carbonyl functions appearing during photo-oxidation are formed by reaction with atmospheric oxygen. Moreover,

the 1600 cm^{-1} band did not shift during irradiation in $^{18}\text{O}_2$, confirming the attribution of the band to an aromatic ring vibration and a change in the ring substitution pattern under exposure, as previously proposed [20]. It was also shown that water can interact with some of the photoproducts. Evidence was obtained showing a hydrolysis of the phenyl formate products giving formic acid that can be extracted from the polymeric matrix. The results reported in this article also provide evidence for an exchange reaction between the oxygen 18 atom of the carbonyl function and an oxygen 16 atom of water (H_2^{16}O) via a gem-diol compound. This experiment confirms the attribution of the carbonyl photoproduct absorbing at 1680 cm^{-1} to a ketone ($^{16}\text{O}_2$ exposure).

Application of the technique to MDMO-PPV:PCBM blends permits discriminating the IR absorption bands of photo-oxidation products from the initial carbonyl band of the matrix, and therefore identifying the products of degradation.

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