

Photo-oxidation of electroluminescent polymers studied by core-level photoabsorption spectroscopy

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The C 1s and O 1s core-level photoabsorption spectra of poly[2-methoxy,5-(2'-ethylhexoxy)-1,4-phenylene vinylene] (MEH-PPV) before and after exposure O₂ and broadband visible light were recorded to determine the degradation pathway for this polymer. The change in the O 1s spectra as a function of exposure demonstrates that the O adds to the polymer chain to form a carbonyl group. Exposure to *only* O₂ or *only* light causes no change in the C 1s or O 1s spectra. In the C 1s spectra, the change in the dependence on the photon angle of incidence after exposure demonstrates that O attacks the polymer at the double bond in the vinyl group thereby altering the extended conjugation of the polymer. © 1996 American Institute of Physics. [S0003-6951(96)02415-X]

Conjugated polymers such as poly(*p*-phenylene vinylene) (PPV), which photoluminescence in the green range of the visible spectrum, have been suggested as possible candidates for the active element in light emitting diodes (LED).¹ Poly[2-methoxy,5-(2'-ethylhexoxy)-1,4-phenylene vinylene] (MEH-PPV) emits in the red-orange part of the spectrum and has the added advantage of being soluble in organic solvents.² Successful LED-type devices using MEH-PPV have been made to operate under laboratory conditions, but the lifetime of such devices is typically measured in tens of hours due to degradation of the active polymer. Further improvements in the use of MEH-PPV depend on understanding the degradation process.

Near edge x-ray absorption fine structure NEXAFS spectroscopy measures the cross section of transitions from core levels to unoccupied electronic states by scanning an incident photon energy through an x-ray absorption edge such as that of the C 1s or O 1s electron shell. Peaks appear in the core-level photoabsorption spectrum when the photon energy corresponds to the energy difference between the occupied core level and an unoccupied electronic state (spectroscopic selection rules withstanding). NEXAFS is a sensitive probe of the unoccupied electronic states of gas-phase molecules,³ adsorbates,³ solid state materials,³ and thin films.⁴ Furthermore, because the x-ray photon beam is linearly polarized, the molecular orientation of samples can be determined by monitoring changes in the NEXAFS spectrum as a function of the angle of incidence between the x-ray photon beam and the sample surface.³ In this letter we

present the C 1s and O 1s NEXAFS spectra of MEH-PPV and demonstrate the changes in these spectra as the sample is exposed to broadband visible light and O₂ for varying periods of time.

A 0.5% solution of MEH-PPV in xylene was prepared for spin-casting onto Si(100) wafers under an atmosphere of dry N₂. The NEXAFS spectra were recorded on beamline 8-2 at the Stanford Synchrotron Radiation Laboratory (SSRL). The base pressure in the spectrometer and preparation chambers was $<1 \times 10^{-9}$ Torr. NEXAFS spectra were recorded with the sample surface at two different angles (45° and 90°) with respect to the x-ray photon beam. The sample was transferred to the preparation chamber where it was exposed to an O₂ atmosphere and/or a source of visible white light for varying periods of time. The light was radiated into the chamber through a glass window to filter out any UV component. After each exposure, the preparation chamber was evacuated and the sample was transferred (*in vacuo*) back to the spectrometer chamber where the C 1s and O 1s spectra were again recorded.

Figure 1 shows the O 1s NEXAFS spectra of untreated MEH-PPV and the spectra of a polymer after a 90 min exposure to (A) 1 atmosphere of O₂, (B) a white light source, and (C) both light and O₂. The monomer unit of the polymer is shown above the curves. As shown by the bottom three curves in Fig. 1, exposure to only light, or only O₂ causes essentially no change in the O 1s NEXAFS spectra of MEH-PPV; only when the polymer is exposed simultaneously to both visible light and O₂ (Fig. 1, top curve) do we observe significant changes in the O 1s spectrum. This is corroborated by a recent publication using a UV source.⁵ The weak

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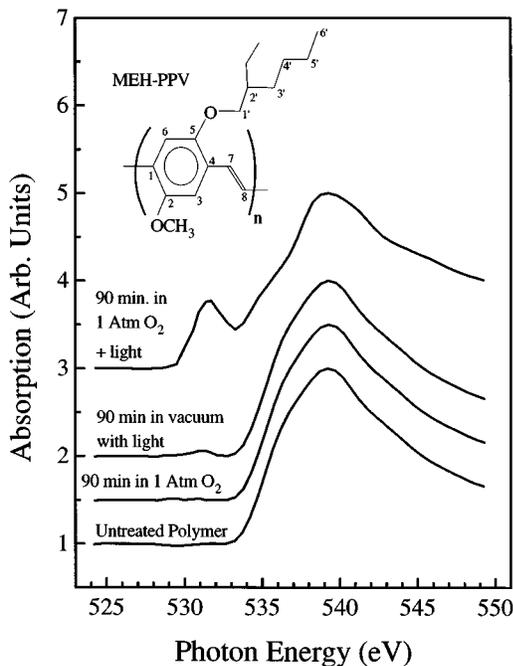


FIG. 1. The O 1s NEXAFS spectrum of MEH-PPV (bottom curve), and after a 90 min exposure to 1 atmosphere of O₂, visible light, and both light and O₂ (top curve). Only the simultaneous exposure to both light and O₂ causes significant change. The monomer unit is shown in the upper left.

feature at 531.5 eV in the spectrum after exposure to light is due to the fact that the O₂ exposure and the light exposure were done sequentially on the same sample. After evacuation of the preparation chamber, some O₂ may have been adsorbed on the sample that then reacted upon exposure to light. From Fig. 1 we conclude that the process of degradation is photo-oxidation.

Figure 2(a) shows the C 1s NEXAFS spectra of MEH-PPV recorded with the sample surface at 90° and 45° with respect to the incident x-ray photon beam. Because the MEH-PPV is a rigid molecule its preferred orientation on the Si substrate is to lie approximately flat⁶ with the *p*-orbitals that form the conjugated π bonds directed perpendicular to the sample surface. Thus, one can enhance the transitions from C 1s to π^* -type orbitals by tilting the sample so that there is better overlap between the electric vectors of the linearly polarized x-ray photon beam and the dipole moment of the molecule. In the 45° spectrum of Fig. 2(a), the enhanced intensity of the two peaks at 284.78 and 287.49 eV mandates that they must result from transitions to unoccupied orbitals of π^* character and demonstrates the highly oriented structure of the sample.

Figure 2(b) shows the C 1s NEXAFS spectra of MEH-PPV after being exposed to 1 atmosphere of O₂ and visible white light for 90 min. The presence of the original π^* transition, now at 285.03 eV, is evidence that the dosed polymer has retained most of its π bonds, but now the spectra recorded at 90° and 45° are essentially identical. The uniformity of the two spectra in Fig. 2(b) can only mean that the dipole moments of these π systems are now randomly oriented. The most likely explanation of this is that the vinyl group (carbon atoms 7 and 8, Fig. 1) has been oxidized, allowing free rotation of the benzene ring about the polymer

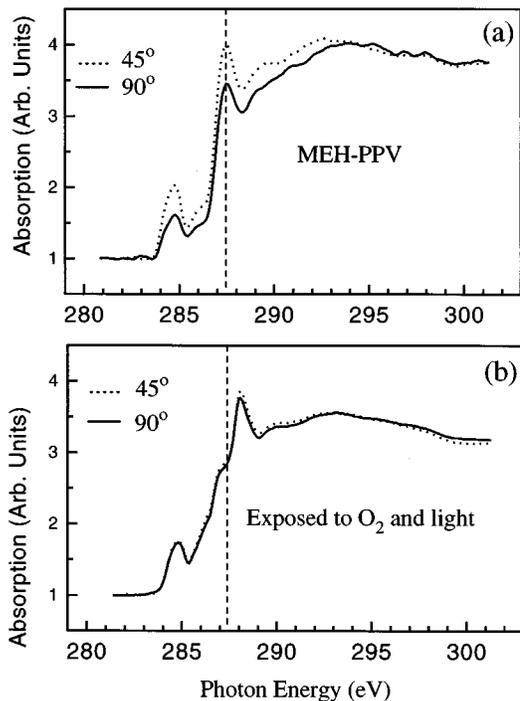


FIG. 2. (a) The C 1s NEXAFS spectrum of MEH-PPV recorded with the sample surface at 45° and 90° with respect to the photon beam. (b) After exposing the sample to visible light and O₂ for 90 min. The absence of angular dependence after exposure demonstrates that the vinyl group becomes oxidized, allowing free rotation of the benzene rings about the polymer backbone. The dashed vertical line at 287.4 eV emphasizes the shift in peak position upon exposure to light and O₂.

backbone. The spectra in Fig. 2(b) have features in common with those of ethyl benzoate⁷ (C₆H₅COOC₂H₅), which suggests ester formation in the polymer chain.⁵ This will be discussed in future publications.⁸

Figure 3 shows the O 1s NEXAFS spectra of MEH-PPV (bottom curve) and three spectra of the sample after successive exposures to O₂ and visible white light. Because exposures were not always done at the same pressure or for the same length of time, the units of exposure are reported in atmosphere-minutes (atm-min). Time constraints prevented complete oxidation of this first sample and so the fifth (top) curve in Fig. 3 was recorded on a different sample of MEH-PPV at a later date. The sharp feature growing in at 531.5 eV is indicative of an O 1s to π^* transition in a carbonyl functional group. This value is commensurate with the position of similar peaks in the O 1s spectra of benzaldehyde⁷ (C₆H₅COH; 531.0 eV), terephthalaldehyde⁷ (HOCC₆H₄COH; 520.6 eV), methyl formate⁷ (HCOOCH₃; 532.1 eV), and ethyl benzoate⁷ (C₆H₅COOC₂H₅; 531.5 eV). In each of these four examples, there is a peak at ~531.5 eV that is assigned to the transition from an O 1s orbital to a π^* molecular orbital associated with the double bonded carbonyl.⁷ The pristine MEH-PPV polymer has no doubly bonded oxygen, thus, the growth of the O 1s feature at 531.5 eV is indicative of the formation of a carbonyl functional group—probably in the form of an ester.^{5,8}

Summarizing, from Fig. 1 we know that the process of degradation is photo-oxidation. In Fig. 2, the absence of angular dependence of the spectra after dosing with visible

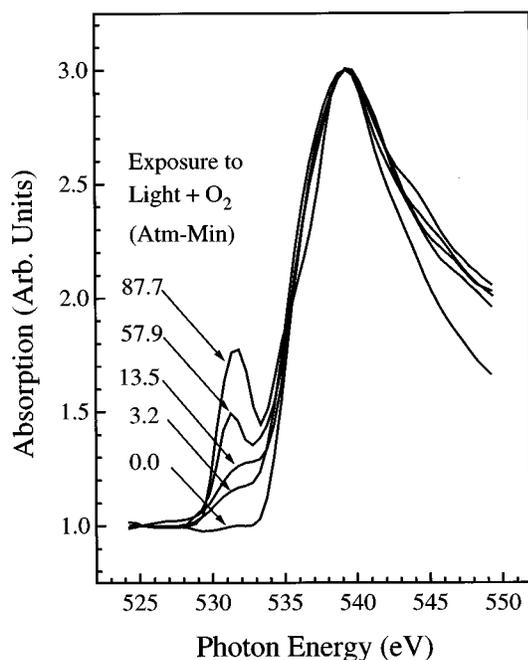


FIG. 3. The O 1s NEXAFS spectra of MEH-PPV (bottom curve) and after successive exposures to visible light and O₂. The sharp feature growing in at 531.5 eV is evidence of the formation of a carbonyl group.

light and O₂ demonstrates that the vinyl group is photo-oxidized. From the O 1s NEXAFS spectra in Fig. 3 we see that exposing MEH-PPV to both O₂ and visible white light introduces a carbonyl functional group into the polymer chain. We conclude that exposing MEH-PPV to both O₂ and visible with light introduces a carbonyl group, probably an

ester, and breaks the double bond at carbon atoms 7 and 8, thereby destroying the extended conjugation in the polymer chain. This chain segmentation is also suggested by a similar photo-oxidation study of MEH-PPV, where a blueshift in the fluorescence spectrum was observed.⁹ This chemical information is valuable to determine the viability of this polymer in commercial applications.

In the time since this letter was submitted, the authors have become aware of similar work by another group using infrared spectroscopy.¹⁰

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