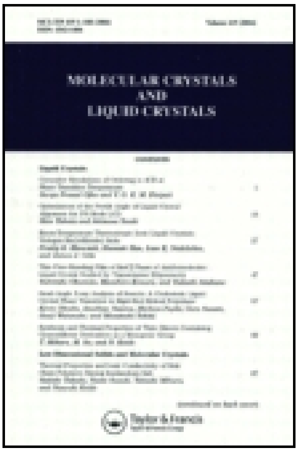

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Photo-oxidation Phenomenon of MH-PPV Films Studied by Ellipsometry and Infrared Spectroscopy

Rodrigo F. Bianchi [a] , Débora T. Balogh [a] , Débora Gonçalves [a] , Roberto M. Faria [a] & Eugene A. Irene [b]

[a] Instituto de Física de São Carlos, Universidade de São Paulo, CP 369, São Carlos, SP, 13566-590, Brazil

[b] Department of Chemistry, University of North Carolina, Chapel Hill, NC, 27599-3290, USA

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Photo-oxidation Phenomenon of MH-PPV Films Studied by Ellipsometry and Infrared Spectroscopy

RODRIGO F. BIANCHI[a,*], DÉBORA, T. BALOGH[a],
DÉBORA GONÇALVES[a], ROBERTO M. FARIA[a] and
EUGENE A. IRENE[b]

[a]*Instituto de Física de São Carlos, Universidade de São Paulo,*
CP 369, 13566-590, São Carlos - SP, Brazil and
[b]*Department of Chemistry, University of North Carolina,*
27599-3290, Chapel Hill - NC, USA

ABSTRACT

In this paper we study the photo-oxidation phenomenon in the structure of a PPV derivative, the poly[(2-methoxy-5-hexyloxy)-*p*-phenylenevinylene] - (MH-PPV), using ellipsometry and infrared spectroscopy techniques. Ellipsometric measurements were carried out in MH-PPV films previously exposed to light irradiation in air. It was observed a variation of both real and imaginary components of the refractive index. These variations are related with the replacement of the vinyl C=C bounds by the carbonyl C=O bounds, as confirmed by the infrared absorption measurements.

Keywords: poly(p-phenylenevinylene); photodegradation; refractive index; ellipsometry; photooxidation.

INTRODUCTION

After the electroluminescent properties of poly(p-phenylenevinylene) - PPV have been reported in 1990[1], this polymer and its derivatives have emerged as promising materials to be used as active material in light-emitting displays[2]. However, the low stability and the short

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[*] To whom correspondence should be addressed: e-mail: bianchi@if.sc.usp.br, FAX 55 16 2715365.

lifetime of their optoelectronic still have obstacles for commercial applications. Several studies have identified oxygen as the main contributor for degradation mechanisms of these structures[3,4], but we have observed that the effect of the oxygen on the structure of these polymers only occurs in the presence of light.

In this work we have focussed on our attention on the photoxidative process of a PPV derivative, poly[(2-methoxy-5-hexyloxy)-*p*-phenylenevinylene] - (MH-PPV). In order to investigate the photooxidative process, we used infrared spectroscopy and ellipsometry techniques, carrying out measurements of the refractive index of MH-PPV samples under illumination in air.

MATERIALS AND METHODS

The synthesis of MH-PPV was performed following a modified Wudl and Srdanov route[5,6] in three distinct steps. In the first step, 4-methoxyphenol was mixed with sodium methoxyde in methanol and reacted with 1-chorohexane for 9 h under reflux. After evaporation, the residue was dissolved in ethyl ether and washed with NaOH 10 % solution and water. After drying, 4-methoxy-1-bis-hexyloxybenzene was obtained. For the second step, the methoxy-hexyloxybenzene was chloromethylated with formaldehyde in HCl at 0 ^{0}C, using dioxane to obtain the dichlorinated monomer. The monomer was then polymerized (step three) at room temperature using potassium ter-butoxide in dry tetrahydrofuran (THF). The polymer obtained was precipitated from THF in methanol. The maximum UV-Vis absorption and photoluminescence emission, molecular weights and polydispersity obtained were, respectively, 510 nm, 640 nm, 133600 g mol^{-1} and 1.9. Solutions of MH-PPV were prepared in chloroform (10 g L^{-1}) and casted on glass substrates recovered with chromium/gold layers and silicon wafers. To remove traces of the solvent, the samples were heated to 50 ^{0}C under vacuum for 30 min. The notations *Au/MH-PPV* and *Si/MH-PPV* refer, respectively, to the polymer deposited on glass/Cr/Au and Si substrates. For *Au/MH-PPV* sample, the film thickness was *ca* 1.1 μm, while for *Si/MH-PPV ca* 0.1 μm.

To investigate the photoxidation mechanism of MH-PPV, the samples were exposure to an intensive polychromatic light in air. The infrared measurements (*FTIR*) were carried out by a *Nicolet 560* equipment from 2000 to 600 cm^{-1} in a *Si/MH-PPV* sample illuminated by light of 250 mW/cm^2. Ellipsometry measurements were performed for *Au/MH-PPV* sample illuminated by a light of 100 mW/cm^2, from 2.1 to 4.1 eV (300 – 600 nm), at a 70° incident angle in a previously described custom-build ellipsometer[7]. The illumination was interrupted only during ellipsometric and *FTIR* measurements.

Spectroscopy Ellipsometry (SE)

Ellipsometry[8] is a sensitive technique that measures the change in the amplitude (Ψ) and phase (Δ) between the parallel (p) and perpendicular (s) components of the incident and reflected monochromatic polarized light at an interface. This measurement can be expressed in terms of the complex reflection coefficient (ρ), using the reflectance (R_p and R_s) for multiple reflection for p and s polarized light, i.e.,

$$\rho = tan(\Psi)exp(i\Delta) = R_p / R_s \qquad \mathbf{(1)}$$

where ρ depends, among other parameters, on the angle (ϕ_o) and energy (E) of the incident light beam. For bulk materials, the complex refractive index (N) i usually obtained directed from ρ, expressed by:

$$N = n + ik = \sqrt{sin^2\phi_0\left[1 + tan\phi_0\left(\frac{1-\rho}{1+\rho}\right)^2\right]} \qquad \mathbf{(2)}$$

where n and k are, respectively, the real and imaginary components of N.

RESULTS AND DISCUSSIONS

Figure 1 shows the real, - $n(E)$, and the imaginary - $k(E)$, components of the refractive index (N) for an *Au/MH-PPV* sample at different exposure times (t). From 2.32 to 4.10 *e*V range, n exhibits a minimum value at about 0.90 (at t = 0), which tends to shift towards higher energies and to increase as t increases. Below 2.32 *e*V, n decreases with both E and t, reaching a stationary value after 200 of continuous irradiation. The k *vs.* E curves, on the other hand, exhibit a maximum peak at about 0.85 *e*V for t = 0, which tends to 0.20 as t increases. An isosbestic point (*I.P.*) is observed at 2.80 *e*V (another is observed in the *n* curve at 2.32 *e*V). It is important to remark that the film is originally red, but it changes to weak orange as *t* increases.

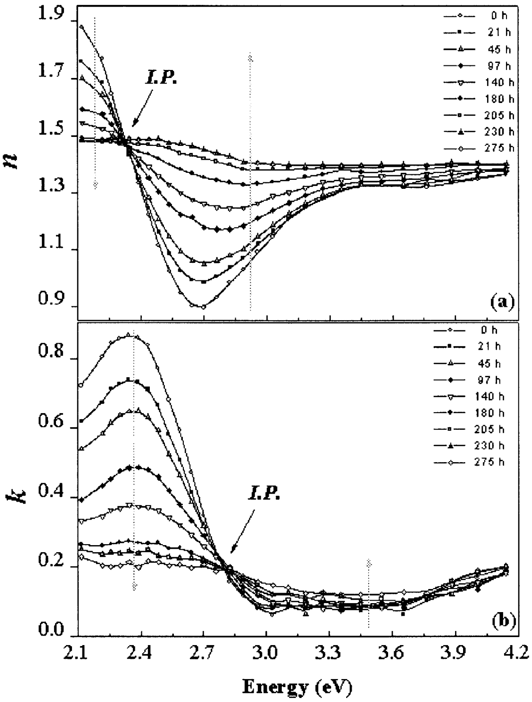

FIGURE 1: (a) *n* and (b) *k* curves for *Au/MH-PPV* as a function of the photon incident energy (*E*) for different illumination exposure times (*t*).

In order to investigate the effect of illumination on the polymer structure, *FTIR* measurements were performed for *Si/MH-PPV* sample at different illumination times, from the 2000 to 600 cm^{-1}, as shown in Fig. 2. It is clear from this result that as *t* increases, the intensity of the vinyl double bond (C = C at 975 cm^{-1}) decreases while the intensity of carbonyl groups (C = O bounds from 1730 to 1600 cm^{-1}) increases.

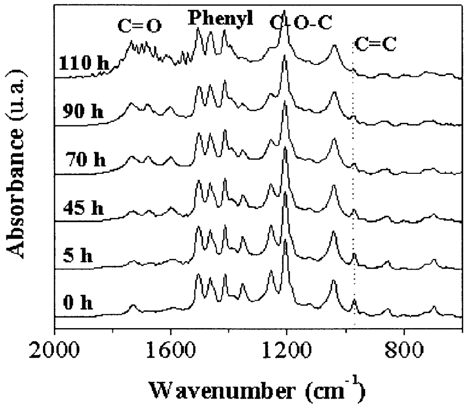

FIGURE 2: FTIR spectra for a *Si/MH-PPV* sample at different illumination exposure times (t).

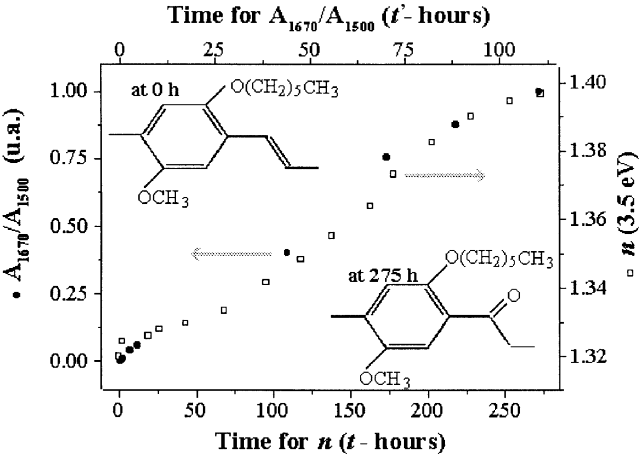

FIGURE 3: n and A_{1670}/A_{1500} as function of illumination time (t).

It was observed that n is almost independent of E, and much higher than k, from the 3.30 to 4.10 eV range (Fig. 1a). Thus, in this range, it is reasonable to consider $N(t) \cong n(t)$. Fig. 3 shows that both n and A_{1670}/A_{1500} (ratio in between the *FTIR* areas of C = O and the aromatic ring absorption at 1500 cm^{-1}) varies equally with the exposure time *t*. This indicates a close correlation of *n* with the variation of C = O bounds. The scales for time axes are not the same due to different intensities of the light used for *FTIR* and *SE* measurements. Fig. 3 also shows the possible monomeric MH-PPV unit at $t = 0$, to a oxidized one after 275 h of illumination. A_{1670}/A_{1500} and n curves equally reach a saturation value at about $t = 250$ h, and an intermediate ration between these two monomeric units is observed in between $0 \leq t \leq 275$ h, forming different comonomer ratio of this random copolymer.

CONCLUSIONS

In this paper we have studied the changes of the complex refractive index and structural composition of MH-PPV films under exposure to light and air. The photo-oxidation is enhanced by a mechanism in which vinyl C = C bounds are replaced by carbonyl C = O bounds, which increases the refractive index from 1.32 to 1.40 in the 3.3 to 4.1 eV range, as the effective conjugation length of the polymer chain diminish.

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