

New Copolymers Containing Charge Carriers for Organic Devices with ITO Films Treated by UV-Ozone Using High Intensity Discharge Lamp

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Abstract: For electroluminescent devices new copolymers were synthesized using a Suzuki cross-coupling reaction based on monomers (fluorene-alt-phenylene) in conjugation with quinoline-alt-phenylene units. They were characterized by ^1H NMR, ^{13}C NMR and FTIR. TGA measurements indicated that the copolymers have good thermal properties and no weight loss was observed up to 250 °C. The UV-Vis spectra were characterized by absorptions from the fluorene-alt-phenylene and quinoline-alt-phenylene segments in the backbone, while their photoluminescence (PL) spectra dominated by emissions from the fluorene excimer. For devices assembly ITO films were treated using a High Intensity Discharge Lamp (HPMVL) without outer bulb presenting high ozone concentration than that conventional germicidal lamp. The device with ITO treated revealed significant decrease of threshold voltage (or turn-on voltage) compared by untreated with I-V curves. This decrease can be related by water and carbon dioxide extracted on surface after UV-Ozone treatment revealed by DRIFT measurements. *Copyright © 2009 IFSA.*

Keywords: Polymer, ITO, UV-Ozone, HID, Electroluminescence

1. Introduction

Polymers are widely used as electrical insulation due to its high electrical resistivity and easy processing. However, since 1963, when it was published the first work on the electrical conduction of conjugated polymers and by at the end of the 1980, it was reported for the first time the electroluminescence (EL) of this class of polymers we have had witnessed the increasing technological and scientific interest on this class of materials [1]. Polymers with fluorene group are very interesting material due to its high photoluminescence (PL), high quantum yields, thermal stability and good solubility. Quinoline is known for its conjugated structures and polymers bearing quinoline groups have been reported to portray a combination of enhanced electronic, optoelectronic or nonlinear optical properties along with excellent mechanical properties [2]. The growing interest in these polymers is due to their technological edge applications such as displays and low cost flat surface devices, good processability and possibility to adjust precisely the emission color. In the present work the Suzuki cross-coupling reaction was used [3]. The synthesis occurs in the presence of a complex formed with the catalyst, for instance palladium (tetrakis(triphenylphosphine)palladium) $(P(Ph_3)_4Pd)$ in which carbon-carbon bonds are formed by coupling a compound containing a borate group and an organo-halide compound. After preparation of polymeric synthesis some devices were mounted. In the assembly of devices were used commercial indium tin oxide (ITO) films as anode deposited on glass due to its good electrical (low resistivity) and optical (transparency) [4]. On the ITO films were deposited: PEDOT:PSS (as Hole Transport Layer)/ copolymer (as emissive polymer described in the next section)/ aluminium (as cathode). Another aspect of great interest for these devices mounted in this work is threshold voltage (or turn-on voltage). To obtain better performance of devices is necessary to have a good emissive polymer or copolymer with surface of ITO film cleaned without undesirable elements [5]. In this work ITO films were treated by UV-Ozone reactor assembled with some components generating low cost. A new copolymer containing fluorene-quinoline groups on the treated ITO film was used. The ozone formed from atmospheric air can be explained by Chapman's cycle [6]:

Table 1. Formation and destruction of ozone by Chapman's cycle.

O_2 (atmospheric air) + $h\nu$ ($\lambda < 243$ nm) \rightarrow 2 O^\cdot (free radicals)	(1)	Ozone formation
$(O^\cdot) + O_2 \rightarrow O_3$ (ozone)	(2)	
$O_3 + h\nu$ ($240 < \lambda < 320$ nm) \rightarrow $O_2 + O^\cdot$	(3)	Ozone destruction
$(O^\cdot) + O_3 \rightarrow 2 O_2$	(4)	

2. Experimental

2.1. Materials Used

All reagents were used as received from commercial sources (Aldrich or Acros) without further purification. The emissive polymer 5,7-dibromo-8-oxyoctyl-quinoline has been synthesized.

2.2. Preparation of Copolymers

The method used is described in the literature. The copolymers were synthesized from 1,4-phenylene-bisboronic acid, 1,4-dichlorobenzene, 5,7-dibromo-8-oxyoctyl-quinoline and 9,9-Dioctyl-2,7-dibromofluorene with tetrakis $P(Ph_3)_4Pd$ as catalyst using two distinct synthetical assessments,

specifically using toluene solution and aqueous calcium carbonate and a modified procedure in which xylene solution and aqueous potassium carbonate, along with a phase transfer agent (benzalkonium chloride).

Shortly, in a dry box under nitrogen atmosphere, a reaction vessel was filled with 0.586 g (1.419 mmol) of 5,7-dibromo-8-oxyloctyl-quinoline, 0.334 g (1.017 mmol) of 1,4-phenylenebisboronic acid (Aldrich), 0.108 g (0.197 mmol) of 9,9-dioctyl-2,7-dibromofluorene (Aldrich, 99%), 0.058 g (0.394 mmol) of 1,4 dichlorobenzene (Vetec, 99 %), 0.034 g (0.034 mmol) of $P(Ph_3)_4Pd$ (Acros, 99 %), all dissolved in toluene or xylene. An alkaline aqueous solution of calcium or potassium carbonate was then added and the reaction mixture was heated up to 100 °C and kept under magnetic stirring for 24 h. After purification 59 % and 88 % of yield were found for copolymer 1 and copolymer 2, respectively. 1H NMR ($CDCl_3$): 8.92 – 8.97 (m, 1H, N-CH), 8.5 – 7.2 (m, 24H, Ar-H), 4.10 – 4.00 (m, 2H, O-CH₂), 2.05 – 1.95 (m, 6H, CH₂), 1.70 – 1.08 (m, 34H, CH₂), 0.89 – 0.77 (m, 9H, CH₃).

2.3. Characterization of Copolymers

1H Nuclear magnetic resonance spectra (200 MHz) were recorded using a Bruker AC-200 spectrometer with deuterium chloroform (Aldrich) as solvent and tetramethylsilane (TMS) as internal reference. The UV absorption spectra were collected by Varian equipment, Cary 50. Samples were dissolved in chloroform and the solution was poured into a 10 mm square quartz cell. The transmission spectrum was collected from 200 – 600 nm. The photoluminescence spectra (PL) in solution were determined using a Varian Eclipse fluorescence spectrophotometer. Samples were dissolved in chloroform and subjected to irradiation at the absorption maximum observed by UV spectroscopy and the emission spectra were collected accordingly. TGA (Thermogravimetric Analysis) curves were obtained using thermal gravimetric analyzer TGA-51 (Shimadzu) in the range from 50 to 800 °C by heating rate at 10 °C / min. under argon atmosphere.

2.4. Analyses of two different lamps for UV-Ozone generation

For UV-Ozone generation were compared two different lamps: a high intensity discharge (HID) or also known as high-pressure mercury vapor lamp (HPMVL) and germicidal tubular fluorescent or also low-pressure mercury vapor lamp (LPMVL).

HPMVL – In the experiment this lamp type was chosen due to its high lifetime operation with $\approx 15,000$ hours, low cost and only some components. In the experiment was used a HPMVL of 400 W with Edison screw without an outer bulb, only ignition tube (quartz tube) connected by aluminium reflector, fans near of wall tube and ballast plugged at local power (220V). The reflector with the lamp was placed upside down insulating ambient of the ultraviolet rays. In the Fig. 1, it is presented the reactor with HPMVL.

LPMVL - In the experiment was used a germicidal fluorescent tubular lamp presenting high lifetime with $\approx 6,000$ hours. This lamp type was also chosen due to its main application of germicidal or sterilization effects destroying bacteria, viruses, mold spores and another organisms. In the experiment was used a LPMVL of 15 W and ballast plugged at local power (110V).

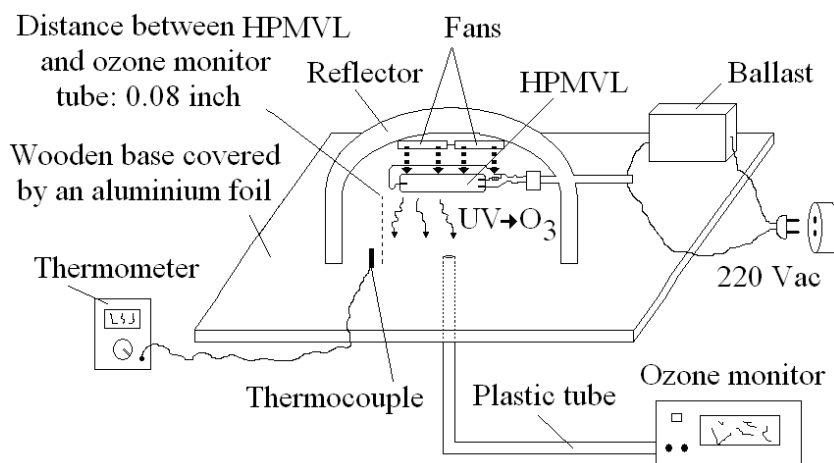


Fig. 1. Reactor mounted with HPMVL and some components for UV-Ozone generation.

This lamp type generally irradiates in specific band of wavelength at 254 nm presenting 100 % of maximum germicidal effectiveness and causing photo-oxidation reactions [7]. How these lamps can cause inflammation or irritation of skin and eyes is necessary to isolate of any closed room. It was connected by electric contacts on wooden base placed into black tube plastic sealed at the two ends. In the Fig. 2, it is presented the reactor with LPMVL.

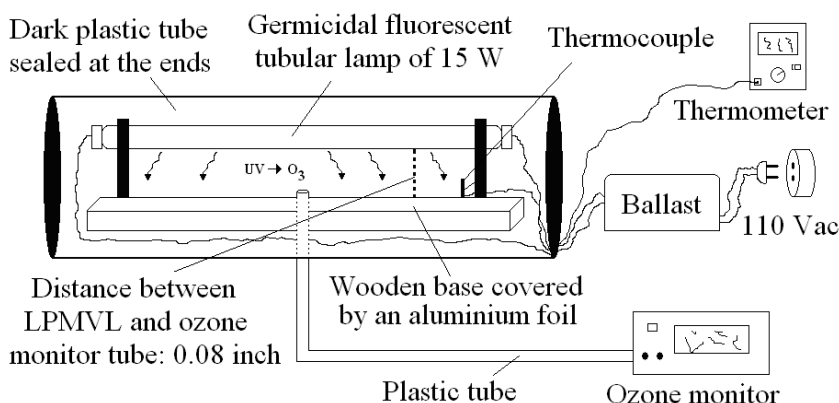


Fig. 2. Reactor mounted with LPMVL and some components for UV-Ozone generation.

The ozone generated by each lamp was collected although of plastic tube connected between reactor and ozone concentration monitor manufactured by In DevR 2B Technologies model 205. A thermometer manufactured by Minipa was also used with thermocouple placed near of the wall lamps monitoring the temperature.

2.5. Preparation of Devices

For preparation of devices with ITO films deposited on glass substrates, the samples were cut in sizes of 1 in². Then the samples were pre-cleaned first into acetone and isopropyl alcohol both each 30 minutes/finally dried with nitrogen flow. After pre-cleaning the substrates were irradiated with UV-Ozone reactor using only HID lamp during 5 minutes.

In assembly of electroluminescent devices polymer and copolymer layers were deposited on ITO films with spin-coating technique by 1,500 RPM by 30 seconds. First was deposited a hole transport layer (HTL) of poly (3,4-ethylenedioxythiophene) doped with poly (styrenesulfonate) (PEDOT:PSS) with ≈ 50 nm thick and annealing by 1 hour at 100 °C and emissive film with copolymer with ≈ 120 nm thick and annealing during 1 day at 50 °C in vacuum both were filtered with 1 μ m porous. The cathode electrode with an aluminium layer ≈ 500 nm thick was thermally evaporated on emissive copolymer. The obtained results were compared between treated and an untreated samples with the analysis revealing influences of treatment on devices.

3. Results and Discussion

3.1. Copolymer Analysis

Fig. 3 shows the ^1H nuclear magnetic resonance spectrum of the copolymer 2. This spectrum was separated into regions to better identification of the peaks. Thus 6 regions were identified; the first region corresponds to the proton more shielded of the end of the alifatic moiety CH_3 . The regions 2 and 3 correspond to the methylene protons CH_2 . Meanwhile, the oxy-methylene protons of the quinoline are in the region 4. The decline in shielding occurs by the proximity of oxygen.

Protons of aromatic rings are shown in region 5 and finally the region 6 corresponds to the deshielded proton on the carbon adjacent to nitrogen.

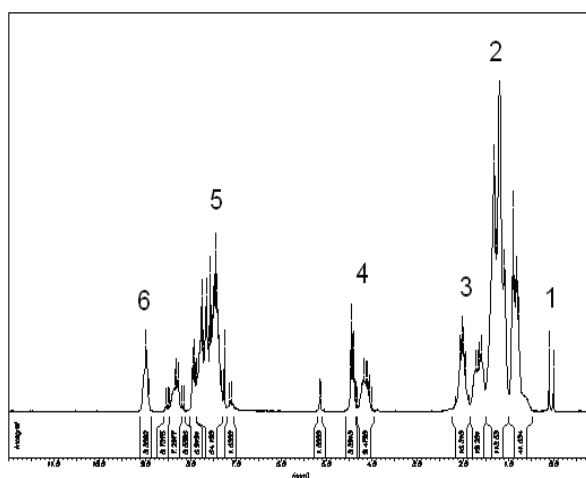


Fig. 3. ^1H NMR spectrum of copolymer 2.

Fig. 4 shows the TGA curves of the copolymers 1 and 2, in the temperature range from 50 to 800 °C. The copolymer 2 presented three steps of degradation. At 250 °C the copolymers begin to decompose. At 386 °C the second step of the degradation of the copolymer and 480 °C the third step.

Fig. 5 shows the absorption spectra of the copolymers 1 and 2 in CHCl_3 . We may notice that for the same molar concentration, both copolymers showed absorption maxima at 250, 280 and 315 nm, varying, however, in their intensity. The intense absorption around 250 nm is due to the phenylene groups of the backbone, while fluorene and quinoline are characterized by absorptions at 282 and 314 nm and 310 nm, respectively.

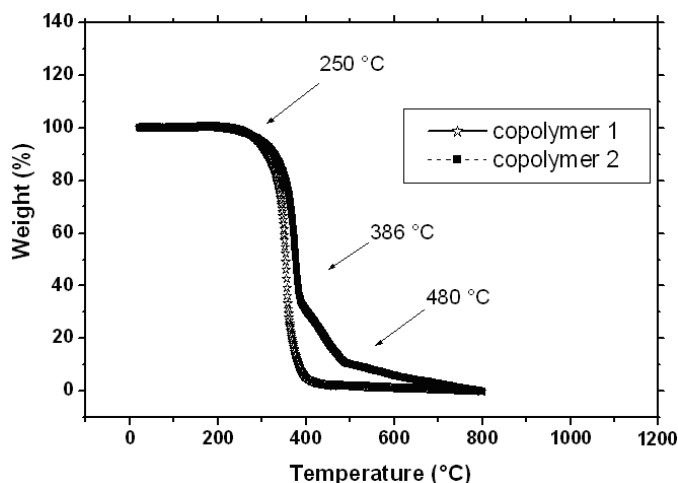


Fig. 4. Thermal gravimetric analyses of the copolymers.

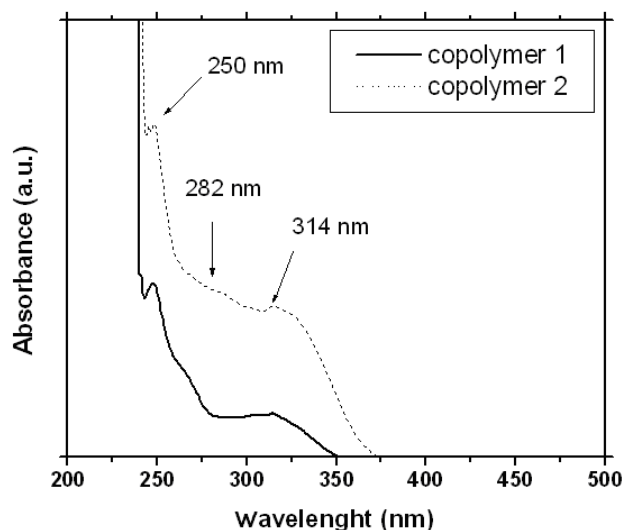


Fig. 5. Absorption spectra of the copolymers.

Fig. 6 shows the fluorescence spectra of copolymers 1 and 2 in CHCl_3 . Both copolymers showed a maximum peak of emission at 419 nm due to fluorene groups, with a little variation in their intensity. No significant emission was observed for phenylene and quinoline groups.

3.2. Lamps Analysis

Fig. 7 shows the ozone concentration vs. time and Fig. 8 shows the temperature vs. time both obtained during eight times in two-by-two minutes until 60 minutes. The arithmetic medium for each point were obtained.

HID lamp presented a faster maximum peak of 0 to 63,000 ppm of ozone concentration during the first 10 minutes of radiation and it shown a decrease to 60 minutes. A possible hypothesis for this behavior can be explained by decreasing of the oxygen amount generated by air inside of reflector that may have been consumed during successive cycles (Chapman's cycle) for ozone formation and also forming sub products of chemical reaction.

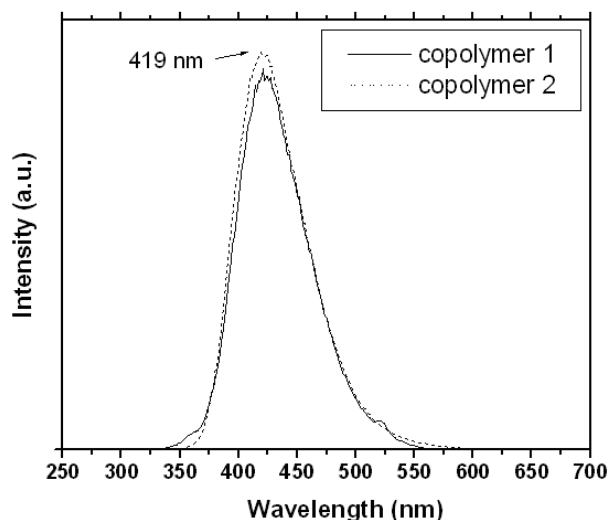


Fig. 6. Fluorescence spectra in CHCl_3 of the copolymers.

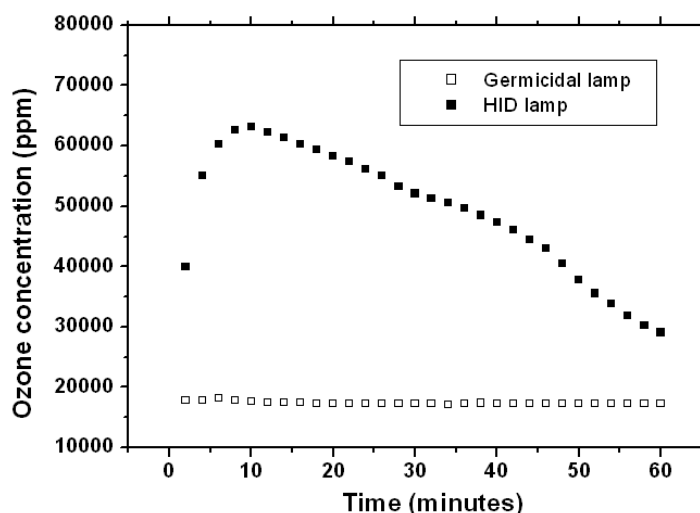


Fig. 7. Ozone concentration vs. time for HID and germicidal analyzed lamps.

Germicidal lamp presented lowest ozone concentration of 0 to 17,000 ppm during all the time of the radiation. Another hypothesis for this behavior can be explained by temperature effect. The germicidal lamp presented temperatures at the 38 °C with low variation, while the HID presented at the 95 °C using fans for maximum time of 60 minutes. The effect of temperature in this case can also contribute with the ozone formation by air atmospheric independent of lamp used.

In the literature is related maximum temperature at 40 °C for better germicidal efficiency of 100 % but it did not report the amount of ozone produced.

The PLEDs assembly was used the HPMVL for generation of UV-Ozone on ITO films and emissive layer with copolymer 2.

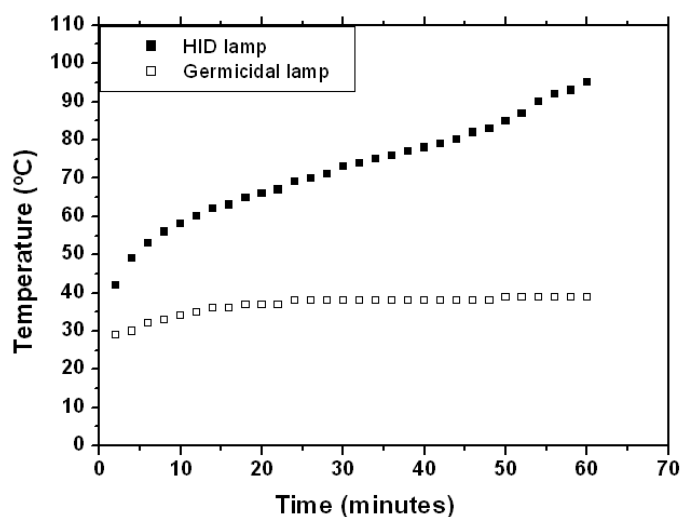


Fig. 8. Temperature vs. time for HID and germicidal analyzed lamps.

Fig. 9 shows the forward bias by current vs. voltage curves for PLEDs devices with ITO films of $85 \Omega/\text{square}$ treated by 5 minutes of UV-Ozone and compared with an untreated sample. The sample treated revealed significant decrease in the threshold voltage (or turn-on voltage) by straight tangent to the curves reaching $\approx 5 \text{ V}$ for treated sample and $\approx 13.5 \text{ V}$ for an untreated sample.

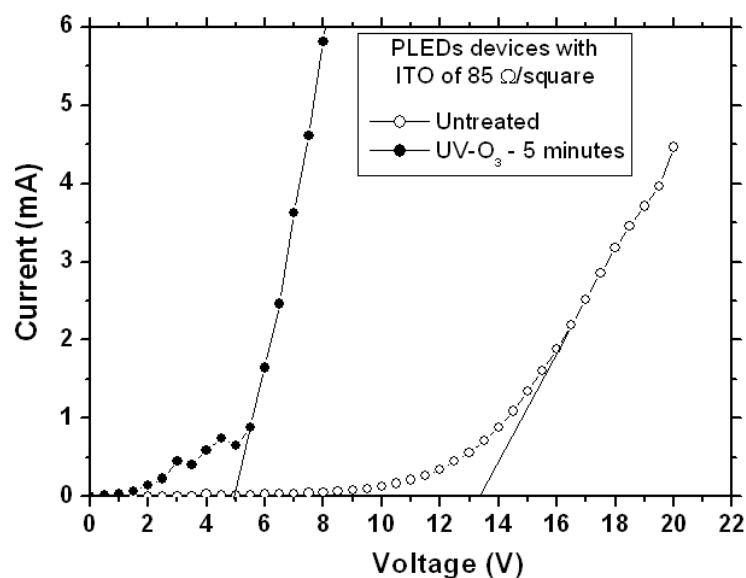


Fig. 9. I-V curves for electroluminescent devices using ITO untreated and treated by 5 minutes of UV-O₃.

Fig. 10 shows the DRIFT (Diffuse Reflectance by Infra-Red Fourier Transformed) technique results. A sample was measured before of treatment and consequently treated by 5 minutes. Before treatment the analysis revealed on surface of ITO film the presence of water and carbon dioxide and after treatment was verified that these elements were eliminated.

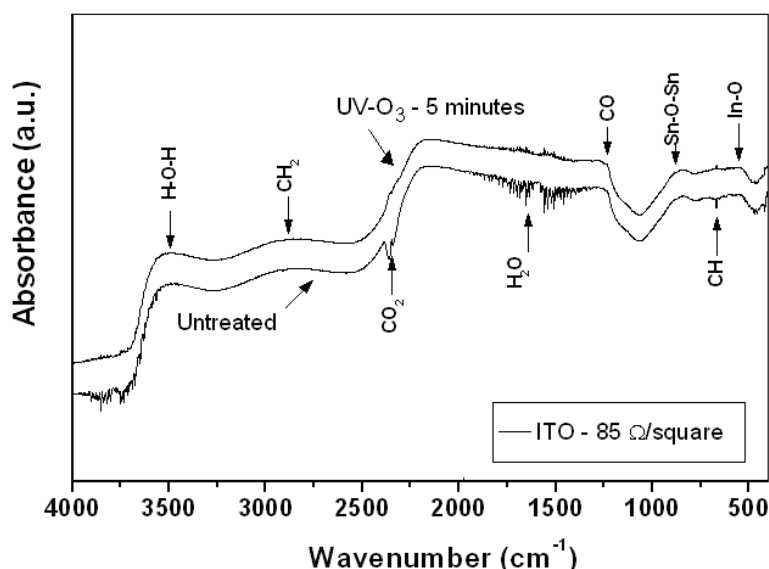


Fig. 10. DRIFT analysis for same sample before an untreatment and after treated by 5 minutes of UV-O₃.

In this experiment was not possible to obtain the luminance of the devices, but a significant change in the surface of ITO film was obtained with the elimination of carbon or hydrocarbon that increases the performance of device treated by 5 minutes as reported in the literature using UV-Ozone with other lamps, commercial equipments or also other methods of treatment [8, 9].

4. Conclusions

Comparative analysis of reactions has shown interesting results indicating fast growth of the chain and, consequently, also an increase in the molar mass of the copolymers prepared by the second route. In that method, it was noticed besides the high yield (>88 %), higher molar mass and during the reaction the solution already presented high viscosity. Compared to the copolymer synthesized by the traditional route, it has been demonstrated improvement in the reaction efficiency. The devices showed no emission of light but presented the typical I-V curves of polymer/organic light emitting diodes.

A new procedure of UV-Ozone treatment using HID lamp was carried out producing highest ozone concentration than that germicidal lamp. For this motive the HID lamp was used for treatment revealing significant difference between an untreated sample and treated by 5 minutes observed by voltage threshold (or turn-on voltage) in the I-V curves. DRIFT measurements revealed the elimination of carbon and hydrocarbon as report in the literature with UV-Ozone using other lamps, commercial equipments or also other techniques of treatment.

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