The influence of UV radiation and ozone exposure on the electronic properties of poly-3-octyl-thiophene thin films

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ABSTRACT

The modification of the conductivity as well as the nanoscale morphology and electrostatic properties of poly-3-octyl-thiophene (P3OT) thin films have been studied as these films are irradiated by ultraviolet light (UV). Films of about 100 nm thickness were prepared by spin-coating a P3OT solution in toluene on glass substrates. The samples were characterized by electronic transport measurements and non-contact scanning force microscopy (NC-SFM) for every cycle of UV radiation. Nanoscale topographic and electrostatic characterization using NC-SFM were performed on the same location using a specially designed sample holder. A two stage degradation process has been observed, the first one presents a chemical modification of the polymer (decoloration of sample) and free carrier mobility reduction, the second one is characterized by a strong structural modification, thickness reduction, oxygen doping and further mobility reduction. The comparison of these results on P3OT with other studies performed on P3HT will allow for a detailed analysis of the role of side-chains in the degradation mechanism upon UV irradiation.

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1. Introduction

Organic solar cells utilize a blend of two conjugated polymers or a conjugated polymer and a fullerene derivative as active layer for efficient solar energy conversion [1]. Apart from the active layer, several polymeric thin films are included in the device in order to improve charge extraction from the active layer towards the electrodes. The most successful class of polymers used as donor material (p-type material in a typical semiconducting junction) are the poly(3-alkylthiophenes) (PAT), which have been intensively studied due to their good environmental stability, favorable processability, and easy modification of optical and electronic properties [2–7]. In the field of organic solar cells the power conversion efficiency and the stability are issues that have to be addressed before this technology can compete with traditional silicon solar cells. The degradation mechanisms of the organic solar cells are now being intensively studied by several groups [8–10]. Many causes of degradation can be roughly organized into two broad groups: a first class of external agents affecting the device performance (contamination by oxygen, water and UV irradiation

have been pointed out as the main causes of degradation) and which can be solved by improved encapsulation and UV filtering, and a second class which are structural or chemical processes occurring in the polymers (bulk heterojunction nanostructure evolution, embedded interlayer roughness modification, diffusion of species between interfaces of different layers, metal contamination from the electrodes, etc.). This second class of processes can be triggered by an external agent, UV irradiation being the most aggressive one, but all are dynamic processes inherently occurring at room temperature in a polymeric device, which does not have a stable configuration at the time scale of months or years. A deeper understanding of the degradation mechanisms of poly-alkyl-thiophenes upon UV irradiation is strongly needed, and accordingly, the means to improve the poor UV light stability and device lifetime is an important field of research [9–11]. The structure of the degraded polymer must be examined for a deeper understanding of the degradation mechanisms which is necessary for the design of long lifetime and UV stable devices. In this article we will focus on poly-3-octyl-thiophenes because the comparison of the behavior of two polymers which only differ in the size of the side chain will shed some light on the proposed mechanism of side chain degradation. Furthermore, solar cells in which P3OT and functionalized single wall carbon nanotubes were proposed, some time ago, as very stable (but not so efficient) active layers for organic solar cells [14,15].

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The main degradation mechanism that we have studied is UV irradiation, but since all the experiments have been performed in air, also degradation of the polymeric films by the generated ozone has to be taken into account. Although ozone is well-known as a degrading agent in polymer chemistry [16–19] and the effect of doping and de-doping processes on the conductivity of P3OT was reported long time ago [20,21], systematic studies on the interaction of oxygen with poly-alkyl-thiophenes in terms of doping and degradation have appeared more recently. The effect of oxygen exposure has been found to have a clear effect in the polymer conductivity, which has been explained by the formation of reversible charge transfer complexes of the oxygen with the polymer which facilitates the generation of carriers upon application of an electric field [22–24]. This results in a p-doping of the polymer, this doping and de-doping process have been found fully reversible in the absence of light [25]. Some authors link this change in the electronic structure of the polymer with morphological changes during the degradation process [10,26,27], but in this case, the changes are no longer reversible. Some mechanisms which explain the irreversible degradation in P3HT point towards modification of side chains of the polymer as one of the main mechanisms of degradation of the active layer [8,12,13]. The effect of side chain length has also been proposed as a mechanism, which explains the different density of states due to differences in effective conjugation length and measured in samples of P3OT sandwiched between metal plates [28]. A different approach to the explanation of the formation of charge transfer complexes uses the concept of trap states created by the inclusion of oxygen in the bulk polymer, these studies use thermally stimulated current and charge extraction by linearly increasing voltage to experimentally measure the intrinsic density of trapped states, which are found to have Gaussian energy distributions with different centers [29,30]. A detailed mechanism has been proposed theoretically to explain the formation of the charge transfer complexes via the hybridization of O_2 and polymer orbitals; in this case, the Fermi level is pushed down into the valence band and pinned with the oxygen band due to charge transfer to O_2, therefore explaining a relationship between the amount of transferred electrons and the ionization potential of the host materials [31,32]. This ionization potential should better be considered as an ionization energy in the case of conjugated polymers, where the HOMO level is a valence band extended to the conjugation length of the polymer and therefore, polymers with a lower HOMO will be more prone to this oxygen p-doping effect.

All these changes may result in an improvement of conductivity by oxygen doping if post-processing treatments are carefully tailored in order to improve the performance of devices in terms of better filling factor and elimination of inflexion points in the IV curves [33].

In this article we have studied thin films of P3OT by means of non-contact dynamic surface force microscopy and electronic transport measurements. The combination of probes which allows measurements at both the nanoscale and the macroscale enables to investigate correlation between the modification of the nanostructure and its impact on macroscopic electronic properties. The electrostatic behavior of P3OT thin film samples by means of electrostatic force microscopy (ESFM) on a nanometer scale and its relationship with the mobility change observed upon UV irradiation are presented and discussed.

2. Experimental

Regioregular P3OT was purchased from Sigma-Aldrich, with 98.5% head to tail couplings, molecular weight M_n=54,000, polydispersity index D=2.6 and density ρ=1.05 g/cm^3 [34]. With the molecular weight of m_{Mol}=194 g/Mol for a P3OT monomer ($C_{12}H_{18}S$) a number density of $n_{P3OT}=\rho/m_{Mol} \approx 3.26 \times 10^{-27}$ particles/m^3 is obtained, corresponding to a volume of 0.67 nm^3 per monomer. P3OT thin films of approximately 110 nm thickness were prepared on glass cover slips by spin-coating a 10 mg/ml solution of P3OT in toluene at 2500 rpm for 90 s in air at room temperature.

UV/O_3 exposure was performed using a commercial 50 W UV/ozone cleaning system from Novascan Technologies (Ames, IA, USA). This system delivers most of its energy (about 50%) into the 254 nm peak and 5% into the more energetic 185 nm peak. For our experimental setup, the samples are illuminated homogeneously with an irradiance of 2.5 kW/m^2 for the main wavelength of λ_0=254 nm, which is about 320 times more UV energy than that delivered by sunlight at AM1.5G standard conditions. The corresponding photon flux is $j_{ph}=I_0/(h\nu_0)=I_0\lambda/(hc) \approx 3.2 \times 10^{21}$ photons/m^2/s.

The experimental setup for the electronic transport measurements is a two probe system, where the current is measured with an electrometer (Keithley Mod. 6514) while a controlled voltage is applied to the sample with a programmable voltage source which acts as an active load (Keithley Mod. 220). Tungsten probes with controlled contact pressure (Süss Microtech probes) have been used together with silver paint in order to improve the contact. The geometry of the samples is bar-shaped, where stripes of P3OT are left after cutting a rectangular P3OT shape on the glass substrates. The silver paint is applied at both ends of the stripes. This configuration allows us to obtain accurate plots of current intensity versus applied voltage, and therefore we can easily obtain a resistance value from linear fits provided that the resistance behaves linearly (ohmic contacts). We used triaxial cables from the electronic equipment to the probes, but the final contact is made using a coaxial cable and the final tungsten tip, therefore, the guard does not contact the probe. Since we are measuring resistance values of the order of mega Ohms, the small voltage drop along the final section of the coaxial and the probe is negligible. All the measurements were performed in air and at room temperature.

A Nanotec Electronica SFM system with a phase locked loop (PLL)/dynamic measurement board [35] was used with Olympus OMCL-AC-type Si cantilevers (nominal force constant: 2 N/m; resonance frequency: 70 kHz). Imaging was performed in non-contact dynamic SFM using the oscillation amplitude as feedback channel to maintain a constant tip-sample interaction, and a small reduction of oscillation amplitude ($A_{set} \approx 0.95$ A$_{free}$) was chosen for feedback. A new precision sample holder integrated in the Nanotec SFM system has been developed for the experiments presented in this work. Essentially, this sample holder allows ex-situ manipulation of the sample and SFM imaging of the same region with a very accurate re-positioning. We can therefore attribute changes of morphology or other properties to a particular effect of UV radiation and/or ozone.

An external lock-in was employed for Electrostatic Scanning Force Microscopy (ESFM) measurements. For the experiments reported in the present work, the tip was biased with a DC voltage (V_{DC}) of 1 V and an AC voltage (V_{ac}) of 0.5 V at an electrical modulation frequency ν_{elec}=7 kHz. The phase shift signal of the mechanical oscillation (measured by the dynamic measurement board) induced by this electrical modulation frequency is the input for the external lock-in used for the electrical measurements [36]. Further details of the ESFM setup and working operation modes are described elsewhere [37,38]. Briefly, we recall that in the (true) non-contact regime, the electrostatic interaction is $I_{elec}(d,V_{tip})= -1/2C(d)(V_{tip}-V_{CP})^2$, where d is the tip-sample distance, V_{tip} the tip voltage, $C(d)$ the capacitance of the tip-sample system and V_{CP} the (local) contact potential between tip and sample. For low