



Side chain structure and dispersity impact the photostability of low band gap polymers



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ABSTRACT

A series of eight low band gap polymers based on benzodithiophene - diketopyrrolopyrrole (BDT-DPP) skeleton were designed with side chain variation on the benzodithiophene unit. The effect of different side chains, including -H, alkyl, alkoxy, and aryl moieties, over polymer stability is examined. Thin films were processed and submitted to photooxidative degradation. We experimentally confirm that alkoxy side chains are the most promising candidates for designing soluble and photo-resistant polymers. This conclusion is modulated by the polymer dispersity which also plays an important role: a low dispersity value being synonymous of higher photostability. The reasons why the side chain structure and dispersity value drive the polymer photostability are discussed. For the design of photo-resistant polymers and devices, side chain selection must go hand in hand with the control of the synthesis meaning a low dispersity.

1. Introduction

Organic photovoltaic (OPV) is a promising technology in terms of competitiveness [1]. Although important efforts have been done especially in terms of device performance, the lifetime remains a crucial point [2]. [3] Indeed, the materials which constitute the active layer of OPV devices are based on organic molecules or macromolecules which are by nature sensitive to combined light exposure, oxygen and humidity [4]. While oxygen and water exposure can be reduced by packaging the devices with barrier materials, it is impossible to completely avoid oxygen diffusion especially when the encapsulation is supposed to be flexible and cost efficient. Therefore, resistant organic materials and a better understanding of the photooxidation mechanism are required.

The photostability of individual materials, especially the one of the most used pi-conjugated donor polymers for OPV application has been investigated in the past: the poly[2-methoxy-5-(3',7'-dimethyloctyloxy)-1,4-phenylenevinylene] (MDMO-PPV) [5], the poly(3-hexylthiophene-2,5-diyl) (P3HT) [6] [7], the poly[N-9'-heptadecanyl-2,7-carbazole-alt-5,5-(4',7'-di-2-thienyl-2',1',3'-benzothiadiazole)] (PCDTBT) [8], the poly[2,6-(4,4-bis(2-ethylhexyl)dithieno[3,2-b:2,3-d]

silole)-alt-4,7-(2,1,3 benzothiadiazole)] (Si-PCPDTBT) [9] [10] and the poly({4,8-bis[(2-ethylhexyl)oxy]benzo[1,2-b:4,5-b']dithiophene-2,6-diyl}{3-fluoro-2-[(2-ethylhexyl)carbonyl]thieno [3,4-b]thiophene-diyl}) (PTB7) [11] [12]. Manceau et al. [13] synthesized donor-acceptor based polymers from various combination of common building blocks and compared their relative photobleaching rates. From the polymers relative stability ranking, some empirical guidelines were then extracted to select the most stable building blocks solely on the basis of the chemical structure. And yet it is well known that other parameters such as the morphological aspect (micro structure and molecular packing) and the purity of the material (defects/impurities from synthesis and processing) are susceptible to influence the material photostability.

First, concerning the morphological aspects, different photostabilities were found for two P3HT of different regioregularity [14]. [7] The regiorandom polymer was found to be less stable indicating that the polymer organization and especially crystallinity plays a key role on the polymer stability. The well-ordered or crystalline domains more resistant to oxidation and oxygen diffusion effects in a similar fashion to simple polyolefins [15]. Still, PBDDTPD thin films obtained from the same polymer batch but processed differently can exhibit different

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photostabilities due to a change of the polymer packing and crystallinity [16]. By increasing the temperature when the polymer is in solution, the obtained polymer film was less structured and therefore less stable when exposed to light and oxygen. Finally, Mateker et al. showed that planar materials forming dense and crystalline films favor the stability of organic materials [17].

Second, about the material purity, Kong et al. [18] observed that performances and lifetime (light and oxygen exposure) of PCDTBT-based devices can be significantly improved by selecting the longest PCDTBT polymer chains. Indeed, they observed that the shortest polymer chains were rich in impurities and charge traps which decreases the initial device performance but also the lifetime. These impurities and traps are probably source of radicals which can participate to the polymer degradation. Mateker et al. [19] also observed that impurities can be linked to the PBDTTPD-based device performance and stability.

Therefore, all these previous studies show that it is not relevant to establish general rule of polymer photostability by only considering the building blocks of the conjugated backbone. In addition, polymers contain solubilizing side chains that can impact their stability. The role of the side chains in polymer photooxidation has been theoretically investigated by H. Santos Silva et al. [20] DFT modelling allowed these authors to design a toolbox of side chains for soluble and photostable conjugated materials.

In the present work, a series of low band gap polymers were designed to clarify the role of the polymer chemical structure by keeping the same backbone composition and varying the nature of the side chains. The selected pi-conjugated backbone is a combination of benzodithiophene (BDT) and diketopyrrolopyrrole (DPP) units as electron donating and electron withdrawing units, respectively. The details of the chemical structure of the eight investigated polymers are shown in Fig. 1. In all polymers, the side chain attached to the DPP unit was kept constant (R2), and the side chain of the BDT unit (R1) was modified according to four variations: (1) no side chain attached (-H atom, P3 and P4), (2) alkyl side chain (-R group, P2 and P9), (3) alkoxy side chain (-OR group, P1 and P8) and aromatic ring plus alkyl chain (-ArR group, P6 and P7). In the case of polymer P4 (-H), the DPP unit was furnished with a longer R₂ side chain for increasing polymer solubility. Alkyl (-R) and alkoxy (-OR) side chains were attached both in a linear version (P1-P2) and in a branched version (P8-P9). Finally, the -ArR group is based on a thiophene (P6) and phenyl (P7) side chain. The polymer films were processed to have equivalent optical density and were exposed to the same degradation conditions (see experimental section). The photobleaching rates were measured and the role of the side chain structure, polymer morphology and polymer properties (Mn, Mw, Đ) on the photostability in air investigated and discussed.

2. Experimental part

2.1. Polymer synthesis

The synthesis and properties of polymers P1, P2, P4 and P6 and their monomers has been previously disclosed [21]. The detailed synthesis routes of the side chains are available in Supporting Information.

Each monomer was thoroughly dried in a vacuum oven overnight prior to use. The DPP monomer (0.500 mmol, 1.00 eq.) and BDT monomer (0.500 mmol, 1.00 eq.) were weighed precisely using a four decimal point balance and added to a dry microwave vial. Fresh tetrakis (triphenylphosphine) palladium(0) (20.3 mg, 0.0200 mmol, 0.0400 eq.) was added to the vial which was then sealed and evacuated then purged with nitrogen three times. Degassed toluene (20.0 mL) and dimethylformamide (2.00 mL) were added to the reaction vessel via a syringe and the reaction mixture was then subsequently purged with nitrogen gas for another 15 min. The reaction was then placed in a 110 °C oil bath and stirred at 800 rpm until the reaction formed a gel

(~1 h). The polymer gels were subsequently precipitated and washed in methanol. The resulting solid polymers were purified by continuous washing via soxhlet extraction in acetone, petroleum ethers (40–60), and cyclohexane. The final green polymers were extracted with chloroform by soxhlet, reprecipitated in methanol and collected by filtration (with exception of polymer P8 which extracted in petroleum ethers). The final polymers were dried overnight under vacuum prior to their characterization. Yields ranged from 87 to 99%.

Polymer P1. 594 mg (99.7% yield) [21].

Polymer P2. 574 mg (99.0% yield) [21].

Polymer P3. 385 mg (93.5% yield)

Polymer P4. 550 mg (94.8% yield) [21].

Polymer P6. 526 mg (87.6% yield) [21].

Polymer P7. 587 mg (97.8% yield)

Polymer P8. 601 mg (98.2% yield, petroleum ether fraction)

Polymer P9. 571 mg (95.5% yield)

2.2. Film processing and photostability evaluation

All polymers were solubilized in *ortho*-dichlorobenzene (10 mg/ml) at 80 °C. Thin films were obtained by spin casting the solution on glass substrates. The spin casting parameters were adapted in order to obtain thin films with comparable UV-vis absorbance at maximum absorption wavelength. This is important as the thickness/absorbance influence the polymer stability [22]. For the polymers P8 and P9, we observed a smaller extinction coefficient leading to a relative low initial absorbance values compared to the other polymers. The polymer films were exposed to the same condition of degradation, in ambient air (30–35% humidity) in a SUNTEST device (from Atlas) equipped with a xenon lamp. The light intensity was 750 W m⁻² in the 300–800 nm domain, and the temperature of the samples was ca. 42 °C.

2.3. Spectroscopic analysis

Changes in UV-vis spectra were followed with a Shimadzu UV-2101PC spectrophotometer equipped with an integrating sphere.

2.4. AFM and XRD

A Nanoscope IIIa atomic force microscope (AFM) from Veeco Instruments was used for surface topography measurement. X-Ray Diffraction (XRD) analyses were made using a PANalytical X'Pert Pro diffractometer equipped with a X'Celerator detector and a Cu anticathode (Kα1/Kα2). The instrument was used in the θ-θ reflection mode, fitted with a nickel filter, 0.04 rad Soller slits, 5 mm mask, 1/16° fixed divergence slit, and 1/32° fixed antiscatter slit. XRD data were measured over a range of 40° (2θ) with a step size of 0.0167° and a total counting time of 3 h.

3. Results

3.1. Polymers photostability

The degradation of polymer thin films irradiated under ambient air conditions was monitored using UV-Vis spectroscopy. Fig. 2 exemplifies such characterization by showing the UV-Vis evolution of P2 throughout exposure to light, together with the corresponding absorbance decay at the wavelength of maximum absorbance. The spectra and the trace of absorbance decrease of all the polymers are available in Figs. S1 and S2 respectively. The absorbance of all polymers decreases versus time of exposure. This effect is irreversible and is a consequence of the evolution of the chemical structure of the polymers when exposed to light and oxygen. The rate of photodegradation of all polymers was extracted from the linear regime of the first part of the UV-Vis loss as shown in Fig. 2b.

Table 1 summarizes the obtained degradation rates for all the

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