

Electronic Supplementary Information

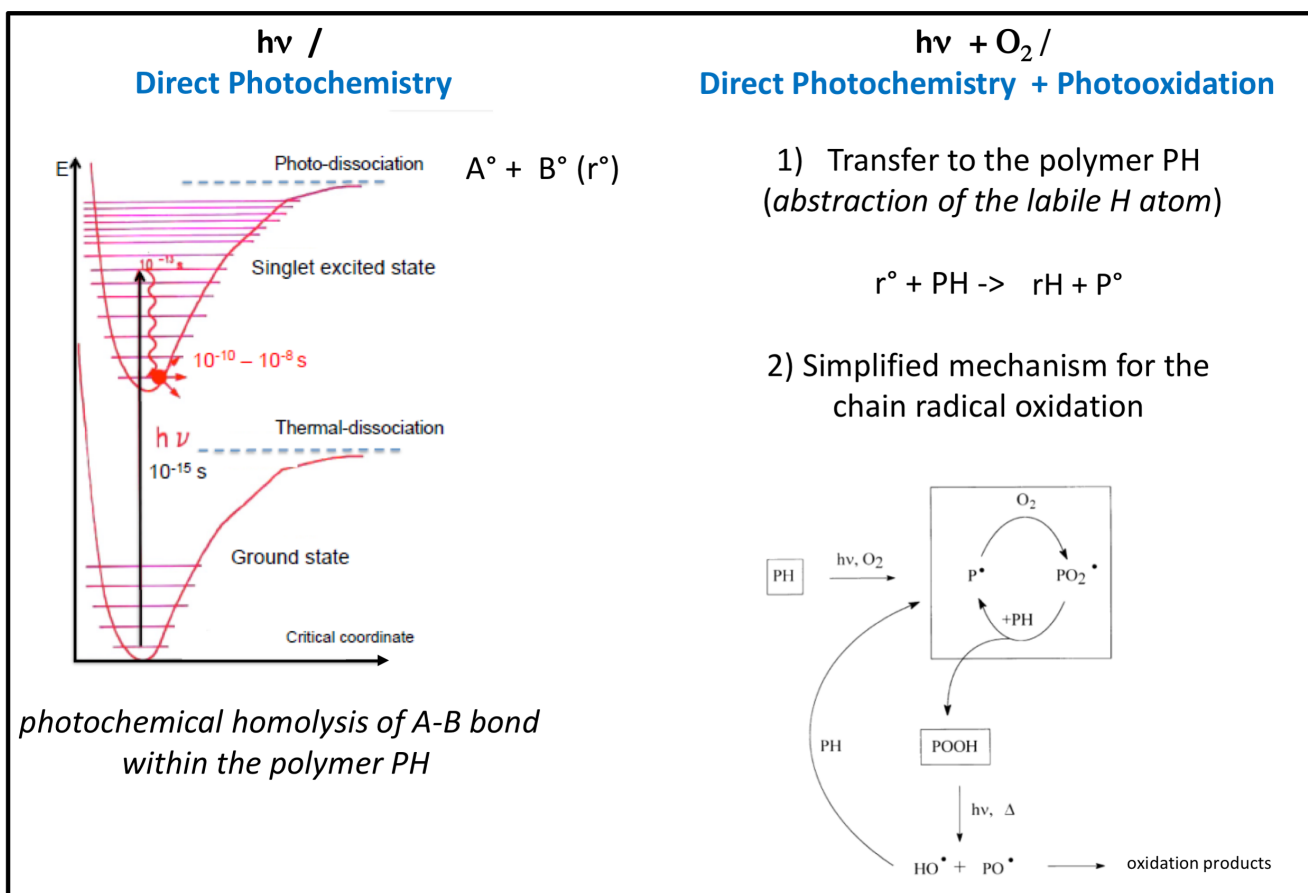
**Designing intrinsically photostable low band gap polymers:
a smart tool combining EPR spectroscopy and
DFT calculations†**

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Scheme S1



Scheme S1. General photodegradation mechanism of a polymer (PH).

The mechanisms by which most macromolecules degrade in air on exposure to UV-visible light are well understood and can be described by a mechanism involving a sequence of steps. The radical chain oxidation of a polymer (PH) begins by hydrogen abstraction of the polymer by a free-radical (r°), that is to say a transfer of the radical to the polymer according to: $PH + r^\circ \rightarrow P^\circ + rH$. To keep it as simple as possible, the photo-oxidative degradation then involves a succession of oxidation and hydrogen abstraction steps. Therefore, the lability of polymer hydrogens towards abstraction is thus a key point in terms of the durability of material properties. The identification and characterization of the labile hydrogen atoms is the first issue that is addressed in this study.

The free-radicals (r°) cited above are produced from photonic excitation of a chromophore within the material. Therefore, a critical issue that has to be addressed is the origin of the radicals which initiate the photooxidation process by abstracting the labile hydrogen atom. Once a photon is absorbed by a chromophore, different process can occur from the excited state; their likelihood of occurrence being

characterized by the *so-called* quantum yield. According to the Jablonski diagram depicted in Figure S1, photophysical (intersystem crossing, fluorescence emission, charge transfer, etc.) and photochemical processes are susceptible: rearrangement, isomerization, homolytical scission. In the latter case, this refers to A-B bonds which can undergo homolytical scission after light absorption: $A-B \rightarrow A^\bullet + B^\bullet$.

The resulting radicals, $A^\bullet$ and $B^\bullet$, could be, of course, the free-radicals, $r^\bullet$, described above that have the ability to initiate the chain radical oxidation process of the polymer, PH, by abstraction of the most labile hydrogen atom. Identification/isolation of photochemical homolysis processes, exclusively, is necessary to determine if the conjugated polymer contains its own intrinsic fragility without requiring extrinsic species to initiate the photooxidation process (superoxide anion,).