



# STABILITY OF POLYMER SOLAR CELLS: A CHEMICAL APPROACH

Polymer solar cells are almost ready to emerge as a viable technology for commercial applications: the efficiencies are constantly growing and new manufacturing methods are cutting the prices down. The stability of these devices seems to be the next big issue to solve. In recent years researchers made great efforts to study and understand the degradative mechanisms of the polymeric materials used for these applications. We can treasure these insights to try to design more stable polymers for photovoltaics.



Polymer solar cells produced by Belectric OPV installed in the German pavilion in EXPO Milan (photo courtesy of Adele Mucci)

**P**roduction of electricity from solar energy is becoming more and more diffuse, and Italy is playing a leading role: in 2014 the country covered the 7.9% of its electrical internal demand by photovoltaic solar cells, which places it at first place worldwide in this ranking. Solar cells made from crystalline silicon are still covering almost the totality of the market share, but researchers are trying very hard to develop new technologies capable of surpassing the intrinsic limitations of the silicon solar cells.

One of the most discussed technologies is the one known under the label of polymer solar cells (PSCs). These cells are characterized by complex architectures, and can be differentiated by a great variety of materials and structural parameters, but they all have in common the presence

of a conjugated, small band-gap polymer in their active layer. A large variety of polymer families has been used in these devices, for example poly(*p*-phenylene)vinylenes, polythiophenes, polyfluorenes, etc. These polymers can all absorb a solar photon and generate an exciton, which can then dissociate to give an electrical current.

The most common architecture for PSC is known as “bulk-heterojunction”. In these devices the active layer is composed of a blend of an electron-donor (the polymer, for example poly-3-hexylthiophene, P3HT) and an electron-acceptor (the most used one is the phenyl-C61-butyric acid methyl ester, PCBM), mixed in a finely interpenetrating matrix so that the interface is large and the efficiency of the charge separation enhanced (Fig. 1).

The great advantages of such a technology, compared to the silicon based cells, are the low cost of the materials, their flexibility, the ease of processability and the independence from limited resources. Unfortunately, it has two major drawbacks that researchers are having a hard time to surpass. The first is efficiency, especially if compared to the more traditional silicon solar cells. The highest quantum efficiency reported so far for single layer bulk-heterojunction polymer solar cells is around 10% [1], which is still quite far away from the 25% of its silicon counterpart. Even if the gap between the two efficiency is still enormous, it is also true that PSC do not have necessarily to compete for the same applications than the silicon solar cells: their field of applications is much larger than the one of the inorganic cells thanks to their flexibility and low weight.

The second and maybe major problem of the PSC is their stability. While silicon solar cells are perfectly capable of surpassing 20 years of field use, PSC have still to demonstrate 10 years stability, even on the laboratory bench. Until few years ago, the attention of the researchers was completely focused on the efficiency of the cells, but now the efficiencies have already reached market feasibility and the stability problem is becoming more and more studied. The “International Summit on Organic

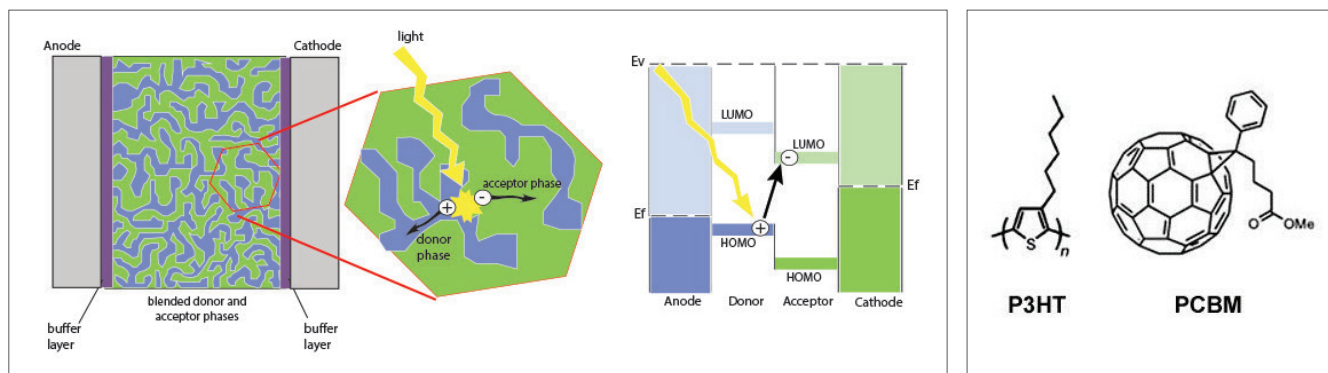


Fig. 1 - a) Scheme of the structure of a bulk-heterojunction solar cell, with energy levels diagram to show the charge separation; b) the molecular structures of P3HT and PCBM

Photovoltaic Stability” (ISOS), that has reached its 8<sup>th</sup> edition this year, is an example of the recent efforts to investigate and improve stability of Organic PhotoVoltaics (OPV), establishing standard testing protocols and initiating focused research on organic solar cell degradation.

When talking of PSC, we can differentiate between two kind of instabilities: extrinsic and intrinsic. Extrinsic instability can be common to different solar cells technologies, and is related to the degradation of the device as a whole (corrosion, fouling, etc.). Intrinsic instability relates to the properties of the specific materials (and of their assemblies) used in the solar cell, and can be again differentiated between chemical or physical degradation (for example, photo-oxidation of the polymer vs. phase segregation of the donor-acceptor blend).

As chemists, our interest is directed towards the chemical processes that drive the degradation of the active polymers: by understanding how they work we can then find a way to block them or avoid them altogether. A big amount of work has been put in this field by the research community, and nowadays there is a fairly good understanding of what are the most common degradation pathways for these polymers.

The fact that the first and most important degradation reaction for these polymers is photo-oxidation is extremely ironic, since these materials are purposely made to be irradiated with the strongest possible amount of light. In the early days of research on organic photovoltaics, it was immediately clear that there was a crucial problem with the stability of the ether substituted poly-phenylenevinylene (PPV) polymers that were used at the time as the “workhorse” materials. The photochemical degradation of this type of polymers has been studied by Chambon *et al.* [2], in a paper where they recognized two main reactive sites on the polymer that could give stability problems: the first one being the side chains on the aromatic ring and the second one being the double bond of the backbone itself. It was later found that these processes are due to the formation of

a radical cation of the polymer [3], formed by a photo-induced electronic transfer between the excited polymer and an oxygen molecule (Fig. 2). The presence of the radical cation then initiates a chain oxidation process by fixation of molecular oxygen or by reaction with a superoxide oxygen anion formed during the radical formation. The result is the extraction of a hydrogen atom at the  $\alpha$ -position of the ether moiety that propagates the chain oxidative reaction.

After the realization of the excessive instability of the substituted PPVs, the attention of the community shifted on a different polymer, luckily much more stable: several studies have been done using (P3HT) as the model molecule. P3HT has become with time the standard of organic photovoltaics: it is the most used conjugated polymer and it is commonly taken as the stone of paragon for new materials. Manceau *et al.* demonstrated that the light-excited P3HT interacts with an oxygen molecule to give a side-chain oxidation reaction, with the formation of an hydroperoxide at the benzylic position [4]. This extremely reactive species can then dissociate, due to light or heat, with the formation of radicals, which can attack the main backbone of the polymer, breaking the  $\pi$ -conjugation. The photooxidation mechanism is extremely similar to the one of the PPVs, but the process is considerably slower.

In another study [5] this photo-oxidative instability was investigated on a wider range of polymers, chosen among the new class of low-band gap donor materials. These polymers have been largely studied in recent years because they are characterized by large absorption ranges of the solar spectrum, that boosts their efficiency in PSCs. They are made by electron-rich and electron-poor monomers in an alternating chain; in this way, there is a push-pull effect that increases electron delocalization along the chain and lowers the band-gap. The results of the study highlight some interesting “general rules” when it comes to the stability to photo-oxidation, and a general stability scale for some of the most

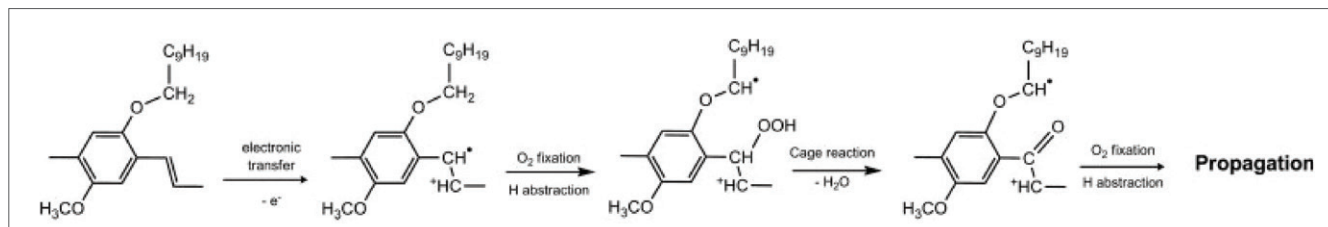


Fig. 2 - Mechanism of the formation and propagation of the radical cation of the PPV. Reprinted with permission from S. Chambon *et al.* [3] (Copyright 2009 Wiley)

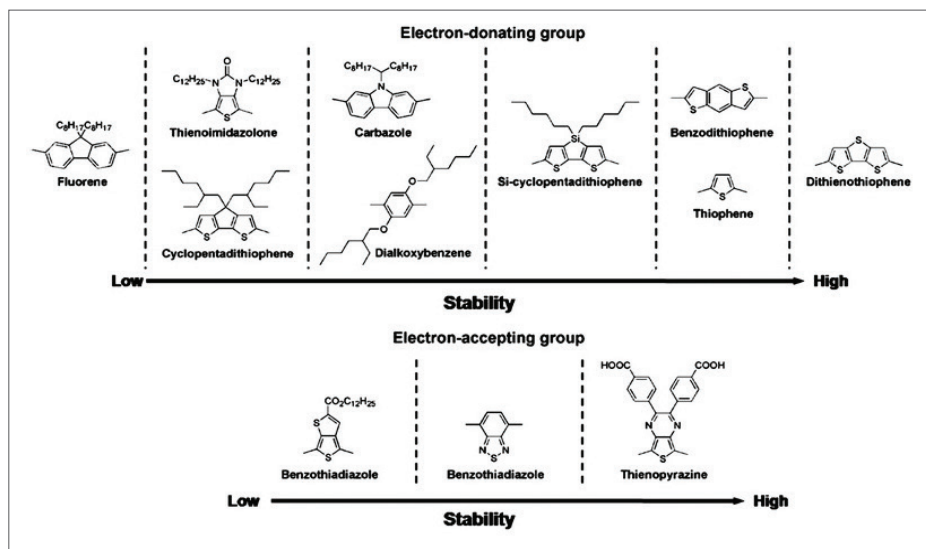


Fig. 3 - Scale of stability for both electron-donor and electron-acceptor common monomers in low-band gap polymers. Reprinted with permission from M. Manceau *et al.* [5] (Copyright 2011 Royal Society of Chemistry)

commonly used monomers (Fig. 3). To obtain these data, the researchers prepared different series of polymers using a combinatorial approach, and then recorded UV-vis spectra of the different films at time intervals during the degradation process. They then extrapolate the relative effect on the rate of photo-degradation of each different monomer.

The study confirms that the side-chain is a weak spot in the stability of the material, since the most stable monomers are the ones without any substituent. Another confirmation of the degradative mechanism can be found considering the low stability of the monomer in the presence of quaternary carbons, which is consistent with the oxidizability scale. It also appears that aromatic polycyclic units help increasing the stability of the polymer.

Side chains, even if they are the main problem for the long term stability, are an important part of these polymers, necessary to impart solubility, thus granting an easy method of process (which is one of the strong point of this technology). Various research groups have thus studied differently functionalized monomers to try to assess a stability scale for the side chain. For example, a study [6] by Xia *et al.* showed the photo-oxidative stability is enhanced by changing the side chain on the acceptor monomer thieno[3,4-b]pyrazine in a scale that goes from -H<-methyl<-octyl<-phenyl. It is very interesting to note that this reflects perfectly the reactivity scale of the radical.

A recent study [7] highlighted the exceptional chemical stability of oxy-alkyl side chains bound to an aromatic group. Since oxygen atoms bound to alkyl carbons were known to reduce the stability towards photo-oxidation, oxygen bearing side chains were discarded in the design of new conjugated polymers. However, after ab-initio calculations, it was unexpectedly found that it is the relative position of the oxygen atom in the side chain that matters. If the oxygen atom is directly bound to the aromatic moiety, its electronegativity can hinder the electronic delocalization on the aromatic ring, rising the energy for radical formation.

Another possible strategy to solve the problem of the side chains was suggested by Liu *et al.* [8], by the introduction of a thermocleavable group on a polythiophene. In this manner the polymer is soluble and

can be casted with ease, and a thermal treatment at 300 °C cleaves the side chain leaving behind a native polythiophene. Polymers produced with this methodology showed an unprecedented stability towards oxygen [9] in working solar cells.

Given that side chains are the main weak spot, what other structural parameters can play a role in the stability of conjugated polymers? One example is the presence of heteroatoms in the ring structure.

Recently a lot of attention was drawn by the high efficiencies shown by solar cells employing Si-PCPDTBT polymer (Fig. 4) as the active layer, where the silicon atom in the fused ring structure helps increasing the crystallinity of the polymer film compared to PCPDTBT. A stability study on this two polymers was conducted by Aygül *et al.* [10], and they showed that the degradation behavior is strongly dependent on the

bridging atom. While the C-bridged polymer is having a constant degradation rate due to photo-oxidation, the Si-bridged one is showing a degradation rate with two different components, the first much faster than the second. Analysis of XPS spectra of the two polymers shows that the two different rates of the Si-PCPDTBT are two different reactions: the fast reaction rate is characterized by the oxidation of the silicon atom, while the slow second rate is related to the oxidation of the polymer backbone. The higher stability of Si-PCPDTBT is then explained claiming an oxygen scavenging role for the silicon atom, thus protecting the backbone.

In another paper, Fraga Dominguez *et al.* [11] study this reaction mechanism in detail, proposing a mechanism of the evolution of the degradation reaction for the Si-bridged polymer (Fig. 5). Again, the weak point appears to be the presence of the side chains, and the tertiary carbon atom is where the chain reaction starts. From here, the degradation continues in the two polymers following very similar paths, until the radical reaches the bridging atom. Here, based on DFT calculations, they show that the radical is strongly localized on the silicon atom and does not move towards the thiophene ring, as opposed to what happens in the other polymer, where this delocalization is more favorable. This claim is also supported by experimental data, where they show that the absorption spectra of the Si-PCPDTBT is less influenced by the photo-oxidation, implying a preservation of the conjugated structure of the polymer backbone.

Not only the structure of the backbone but also the length of the polymer chains plays a crucial factor for the stability of the PSCs. Kong *et al.* [12]

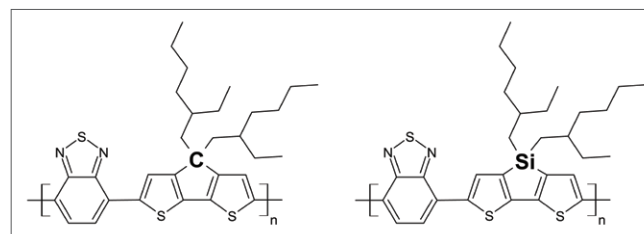


Fig. 4 - Structure of PCPDTBT and Si-PCPDTBT

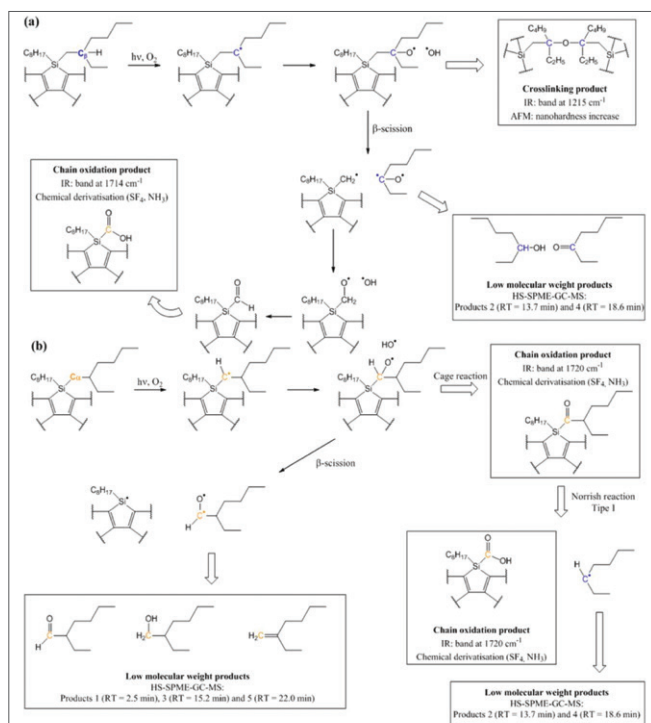


Fig. 5 - Mechanism of photooxidation of Si-PCPDTBT. Reprinted with permission from I. Fraga Domínguez *et al.* [11] (Copyright 2015 American Chemical Society)

show in a recent work that, exploiting a differential solvent extraction at various temperatures, they were able to separate an almost unimodal distribution of high molecular weight polymer chains. Devices prepared with only this high weight component showed a dramatic increase in both efficiency and stability when compared to the devices prepared with the non-purified polymer. The researchers claim that the reason for this behavior is a lower concentration of traps in the material (a trap is an energy state in the band gap, usually created by a light-induced reaction, that can help recombination of the exciton and thus decrease the efficiency), allowing for a reduced “burn-in” loss. Namely, the “burn-in” is the loss in efficiency that PSCs experience in the first few hours of working time under light exposure, and it has been related [13] to the reactions occurring between impurities in the polymer or the chain ends with oxygen trapped in the polymer film.

The same effect in reducing the burn-in loss is seen when looking at the difference in crystallinity of similar polymers [14]. For example, the burn-in loss for a device built using a regio-random or a regio-regular P3HT is respectively 12.4% and 5.5% after 60 hours of illumination, and the main difference between the two polymers is their aggregation state, which is amorphous for the former and crystalline for the latter. From the measurement carried out on these materials, Heumueller *et al.* show that the presence of light-induced traps is common between the two polymers, but that the highly crystalline one is more resistant to their influence. They claim that this behavior is due to the increased charge separation efficiency in the crystalline material: since there is a driving force for the charges to leave the amorphous region and migrate into the crystalline phase, and since electron and holes will occupy respectively the polymer and the fullerene phase, the charges have a minor probability to recom-

bine. On the contrary, in the amorphous material the active layer is made mostly of mixed phase, and the charges will have an increased probability of recombination. The hypothesis is that this charge separation in the crystalline material helps avoiding the traps-induced recombination, but this mechanism is still under investigation.

None the less, it is clear that even more stable, optimized materials will still be inherently sensitive to oxygen and water. The ultimate strategy to preserve the efficiency of these PSCs during their lifetime is to use an encapsulation barrier, but this can prove problematic. The need to maintain the flexibility of the device, which is one of the main selling point of this technology, limits the possible materials that can be used and, of course, the encapsulation needs also to be transparent and cheap. To the present day, encapsulation is the most costly part of the whole production process of commercial OPVs, and these are still far from being able to work without it.

However, even if there is still a long way to go before arriving to stable PSCs, we have to remember that lifetimes came a long way from the start of this technology, jumping from minutes-long functioning devices to bench lifetimes of years in just a decade of research. Now that the attention on this subject is very high, it is feasible that development will accelerate. Maybe we are closer than we think to significant market applications.

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**Stabilità delle celle solari polimeriche: un approccio chimico**

Le celle solari polimeriche sono molto vicine a diventare una tecnologia appetibile per applicazioni commerciali: le efficienze di conversione sono costantemente in crescita e nuovi metodi di produzione stanno riducendo drasticamente i costi dei dispositivi. L'ultima criticità da risolvere è il tempo di vita delle celle in condizioni di uso reale, ancora troppo corto se paragonato con le celle a base di silicio. Negli ultimi anni i ricercatori hanno dedicato molte attenzioni allo studio e alla comprensione dei meccanismi degradativi dei materiali polimerici utilizzati in queste celle solari. Partendo dai risultati ottenuti dalla comunità scientifica, si possono dedurre alcune linee guida generali per il design di materiali più stabili per il fotovoltaico.