University of Groningen

Stability issues of conjugated polymer / fullerene solar cells from a chemical viewpoint

Hummelen, J.C.; Knol, J.; Sánchez, L.

Published in:
EPRINTS-BOOK-TITLE

IMPORTANT NOTE: You are advised to consult the publisher's version (publisher's PDF) if you wish to cite from it. Please check the document version below.

Document Version
Publisher's PDF, also known as Version of record

Publication date:
2001

[Link to publication in University of Groningen/UMCG research database](#)

Citation for published version (APA):
Hummelen, J. C., Knol, J., & Sánchez, L. (2001). Stability issues of conjugated polymer / fullerene solar cells from a chemical viewpoint. In *EPRINTS-BOOK-TITLE* University of Groningen, Stratingh Institute for Chemistry.

Stability issues of conjugated polymer / fullerene solar cells from a chemical viewpoint

J.C. Hummelen[*], J. Knol, L. Sánchez

Stratingh Institute & Materials Science Center, University of Groningen, Nijenborgh 4, 9747 AG Groningen, The Netherlands

ABSTRACT

The efficiency of energy conversion and the stability or lifetime of 'plastic' photovoltaic cells, based on conjugated polymer/ fullerene blends, are the two main issues to be improved for this type of devices. The stability of these PV cells depends potentially on a large number of factors. A brief layer-by-Iayer overview of these factors is given, with main emphasis on the factors possibly playing a role in the active photovoltaic layer consisting of the interpenetrating network of a conjugated polymer and a fullerene derivative.
Complicated sets of photochemical processes can take place in the pure materials and in the donor-acceptor blends, both in the absence and in the presence of oxygen. Especially, photochemical [2+2] cycloaddition and cycloreversion processes have been observed for fullerene derivatives and in certain mixtures containing an oligomer and a fullerene derivative.
These and other (photo) chemical processes are very likely to have an influence on the performance of the photovoltaic cell.

Keywords: bulk-heterojunction, photovoltaics, fullerenes, conjugated polymer, cycloaddition, stability, dimerization, stilbenes, PPV, oxidation

1. INTRODUCTION

Organic photovoltaic (PV) devices based on polymeric materials have received steadily increasing scientific attention during the last ten years.[1] The potential advantages of such 'plastic solar cells' over the present commercial cells are the expected low cost of manufacture and their mechanical flexibility. Especially the bulk-heterojunction version of such cells has received much attention recently. In this type of device, a blend of an electron donor (for example a pi-conjugated polymer) and an electron acceptor (for example a fullerene derivative) serves as the active PV layer.[2] Fundamental steps in molecular solar power conversion are: a. absorption of light; b. exciton migration to the donor-acceptor interface; c. electron transfer; and d. charge carrier transport to the corresponding electrodes of the solar cell. Very recently, influencing the morphology of the bulk heterojunction layer by simply changing the spin coating solvent resulted in a substantial increase of the PV power conversion efficiency to a record value of 2.5 %.[3] A more intimate mixing of the components most likely resulted in both a larger internal donor-acceptor interface area (shortening the exciton transport) and increased percolation of at least one of the components (aiding charge carrier transport on the microscopic scale). Charge carrier transport in the polymer phase was further improved on the mesoscopic scale due to enhanced polymer inter-chain interactions.

Until now, (macro) organic solar cells have shown only moderate stability when sealed rigorously. Even in an inert atmosphere (in a glove box), some degradation is usually observed already within a few hours of operation up to now. Yet, research in the field of organic photovoltaics has been directed almost exclusively towards improving the power conversion efficiency of the devices. In this contribution, we address some chemical and physical aspects of bulk-heterojunction plastic solar cells that can play a role as parameters that influence the power conversion efficiency. Our main interest is in the stability aspects of the active photovoltaic layer, the bulk-heterojunction consisting of (at least) two molecular electronic components: the donor and the acceptor. These components may be present in the form of a blend of two types of molecules, e.g. a conjugated polymer as the donor and a fullerene derivative as the acceptor or two conjugated polymers of which one serves as the donor and the other as the acceptor.[1,2] Bulk-heterojunction photovoltaic layers have also been made using a single component. In that case, molecular dyads were used in which one part of the molecule serves as the donor and another part as the acceptor; hence, the donor and acceptor are covalently linked.[4,5] Other types of donor-acceptor

[*] Corresponding author. E-mail: j.c.hummelen@chem.rug.nl; telephone: (+31) 50 3635553; fax: (+31) 50 3634296; http://www.fwn.rug.nl/solar; http://rugth30.phys.rug.nl/msc.html

architectures are currently under investigation. For example, a number of collaborating European research groups report at present on the preparation of so-called 'double cable' materials, in which a donor and an acceptor component have been coupled in such a way that an array of (fullerene) acceptors is present parallel to a conjugated polymer chain.[6] All of these forms of bulk-heterojunction cells have the following three types of domains in the active layer: the donor domain(s), the acceptor domain(s), and the donor-acceptor interface domain(s). Furthermore, the types of donor and acceptor (sub) structures used have been based on conjugated polymers or oligomers and fullerene derivatives. Therefore, they are likely to have at least a number of (photo) chemical stability issues in common.

2. A GENERAL LAYER-BY-LAYER OVERVIEW

2.1. Some Typical Device Architectures of Bulk-Heterojunction PV Cells

A minimal device architecture for a bulk-heterojunction cell comprises an active donor-acceptor layer, sandwiched between two electrode layers (Figure 1a). The two electrodes preferably have different work functions, since this difference externally induces an electric field in the bulk-heterojunction. Such an electric field, in turn, directs the photogenerated charges towards the respective electrodes to be collected. Usually, a transparent conducting oxide (TCO), in the form of a thin layer on a substrate material (e.g. glass or, as an example of a mechanically flexible substrate, poly(ethylene terephthalate), PET[2d]) serves as the top electrode. In general, since TCO's are high work function materials, a low work function metal is taken as the counter electrode. A thin layer of aluminum (Al) commonly serves as the counter electrode, but other metals and alloys have also been used. In such devices, the photogenerated holes are collected at the ITO electrode, and the electrons at the Al electrode.

More recently, more complicated device architectures have been developed. Most of the extra layers have been added to the basic structure after they were introduced in the field of organic light emitting diodes. A layer of commercially available highly conducting poly(3,4-ethylenedioxythiophene)-poly(styrenesulfonate) (PEDOT:PSS), is often applied between the TCO and the photoactive layer.[2d,e,3] In principle, this PEDOT:PSS layer replaces the TCO as the (PV layer contact) electrode (Figure 1b). One of the advantages of applying this conducting polymer is that an improved interface between the active PV layer and the top electrode is obtained. This results in improved charge exchange (through that interface) with the electrode. However, its use also introduces a new organic component and two new interfaces replacing the PV layer/TCO one to the device.
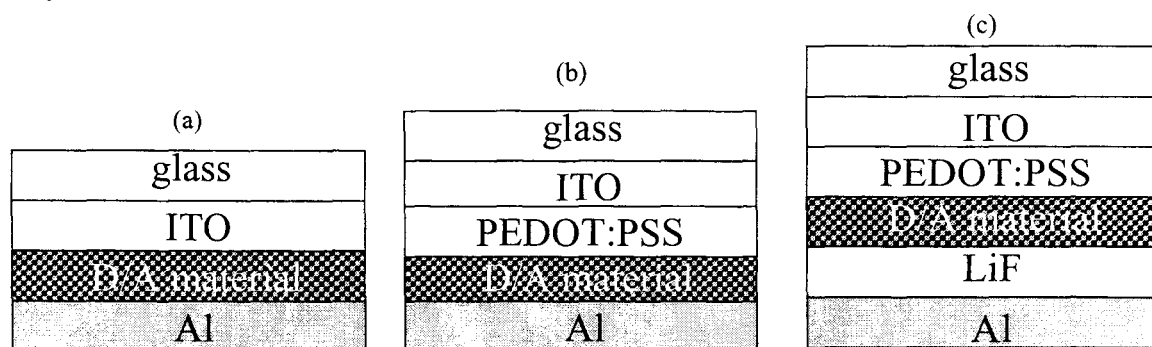
Figure 1. Examples of conjugated polymer/fullerene bulk-heterojunction photovoltaic device architectures on (glass or PET) substrates. A basic three-layer structure (1a); a four-layer structure with a PEDOT:PSS electrode layer (1b); and a five-layer structure with both a PEDOT:PSS electrode layer and a LiF tunnel barrier layer (1c).

Ultra violet photoelectron spectroscopy (UPS) measurements on thin layers of conjugated oligomers or [60]fullerene on metal surfaces have shown that charge transfer takes place between the first organic monolayer and the metal.[7] A vacuum level misalignment and concurrent formation of a dipole layer was observed. Such dipole layers can hinder the charge injection at that interface, which in turn leads to charge recombination. In order to prevent the formation of such dipole layers between either the conjugated polymer or the fullerene component and the low work function metal in the bulk-heterojunction PV cell, a very thin layer of lithium fluoride (LiF) has been applied as an intermediate between the

aluminum electrode and the active layer of the solar cell.[3] Previously, the use of such a layer had been proven beneficial for the efficiency of a polymer light emitting diode.[8,9]. With both a LiF layer and a PEDOT:PSS layer present, the PV device architecture becomes a five-layer structure shown in Figure 1c.

2.2. Stability issues related to the 'passive' layers and interfaces

In principle, numerous processes at different locations in the PV cells could be playing a (more or less relevant) role, in additive, cooperative, competing, or even compensating manners. Usually, workers in the field speculate in terms of oxidative processes and possible chemical processes taking place at the interface(s) between the organic materials and the electrode(s). In order to avoid oxidation, rigorous exclusion of oxygen and water is regarded as a must. Sealing materials are to play a major role in protecting the devices. Therefore, both the initial sealing properties and the environmental stability of these materials will be crucial for the lifetime of the cell. We will, however, leave these materials out of consideration in this study, together with the outer surface and bulk stability properties of the substrate and TCO. Supposing that the solar cells can be effectively protected from oxygen and moisture, all parts of the cells obviously still have to be stable under anaerobic working conditions, i.e. photochemically stable under $1000W/m^2$ sun light irradiation and thermally stable up to ~ 80 °C.

The low work function electrode is prone to oxidation by traces of oxygen and/or water. Oxidation of Al already occurs during the vacuum deposition process of the material. At the metal/blend interface, organometal compounds may be formed during the deposition.[10] These compounds may readily oxidize to yield secondary degradation products. Permanently charged molecules at the metal interface are expected to be more reactive than the bulk material. Although the new Al/LiF and LiF/blend interfaces may lead to their specific stability issues, with the introduction of a thin LiF layer, as in the device shown in Figure 1c, the latter of the above mentioned degradation mechanisms are expected to be strongly diminished.

At interfaces between two organic layers of single materials or blends, thermally activated diffusion processes can take place. At the PEDOT:PSS / MDMO-PPV:PCBM[11] interface, the relatively small PCBM molecules are expected to be the most mobile ones. Such diffusion processes have also been used in plastic PV device fabrication in order to obtain stratified or gradient composite layers. In that case, rapid diffusion was obtained in the presence of a (evaporating) solvent.[12] Polymer chains of one layer may slowly penetrate the other matrix as well, depending on the compatibility of the materials.

2.3. Stability issues of the bulk-heterojunction layer

The bulk morphology of the blend of a conjugated polymer and a fullerene derivative is primarily formed during and directly after the evaporation of the solvent during spin coating or the 'doctor blade' deposition technique. The nature of the solvent and the temperature play an important role in this phase separation process. The morphology of the blend plays a crucial role in efficient charge generation and charge carrier transport. The domains of the two constituents of the blend have to form interpenetrating networks on the scale of the exciton diffusion length in the light-absorbing component. The morphology of the blend has to be thermally stable (up to ~ 80 °C!) in order to prevent further phase separation into larger and/or non-continuous (island) domains.

In the bulk-heterojunction, three types of domains can be distinguished: the (bulk) donor domain, the (bulk) acceptor domain, and the contact (interface) area between these domains. Chemical degradation processes in these domains can be further divided in 'aerobic' / 'anaerobic' and dark / photochemical. While oxidative photodegradation of conjugated polymers has been studied in more detail, there are very few reports on the photo oxidative degradation of a PPV/methanofullerene blend.[13] This blend showed higher stability in comparison with the pristine polymer. It was concluded that efficient quenching of the electronic excited states of the polymer by ultra-fast photoinduced electron transfer to the methanofullerenes protects the polymer from reaction with oxygen. However, such degradation is expected to depend not only on the chemical structure of the components, but also on the morphology of the blend. Fullerenes slowly react with oxygen in the presence of light.[14,15] [60]Fullerene can also act as a very efficient singlet oxygen sensitizer.[16] Hence, when the morphology of the blend is as such that triplet excited fullerene can be formed without immediate quenching through electron transfer, (e.g. in a blend with relatively 'wide' and/or large isolated fullerene domains), photo-oxygenative (singlet oxygen initiated) degradation can, in principle, readily occur in the presence of traces of oxygen. More recently, the transformation of oxygen into super oxide anion (O_2^-) trough electron transfer by C_{60}^- radical anion was described.[17] Hence, in an efficient conjugated polymer/ (methano) fullerene PV blend, i.e. a blend in which (methano)

fullerene anion radicals are formed in high yield by photoinduced electron transfer, formation of super oxide anion and subsequent degradation of blend materials by attack of $O_2^{\cdot-}$ could play a role in the presence of oxygen.

A more fundamental and inherent stability issue is related to the possible dark and photochemical reactions of the constituents of the blend in the absence of oxygen and moisture. Chemical reactions that influence the electronic properties of the materials will eventually lead to changes in the device performance. Since the electronic function of all molecular materials for light harvesting and photovoltaic energy conversion takes place through the more or less extended π electron system parts of the molecules, the photochemical stability of these parts is most important. Photochemical cycloaddition reactions are quite common for non-aromatic π-systems, while aromatic π-systems are less reactive. Such reactions can take place efficiently in the solid state. Both PPV type conjugated polymers and fullerenes contain non-aromatic C=C double bonds in their functional parts of the molecular structure. Hence, a priori, photochemical cycloaddition reactions pose a serious threat to these materials. We have investigated the reactivity of PPV type oligomers and C_{60} in [2+2] cycloaddition reactions. In principle, this type of reaction can take place in all three domains of the blend, leading to domain specific products. Some of our findings are presented in the next paragraph.

Next to ground state and excited state chemical stability, the molecules must be chemically stable in the respective charged states that are formed upon the initial photoinduced electron transfer and during the charge carrier transport through the PV blend. As a rule, both radical cations and radical anions are rather unstable species that readily rearrange or react. Dimerization of radical anions of fullerenes as well of radical cations of conjugated oligomers is known: some salts of [60]fullerene are in the form of σ-dimers, while reversible formation of so-called σ- or π-dimers of oxidized oligomers is a well established phenomenon.[18] Recently, the formation of such π-dimers was observed in chemically oxidized fulleropyrrolidine-oligo(thiophene)-fulleropyrrolidine triads.[19]

3. [2+2] CYCLOADDITON REACTIONS WITH FULLERENES

3.1. Photochemical inter-fullerene [2+2] cycloaddition

In the fullerene domain of the bulk-heterojunction blend, the individual fullerene moieties preferably have to be in close contact in order to facilitate the electron transport through that phase. We have proposed that the use of linear fullerene arrays, like regular and well-defined fullerene containing oligomers or polymers could serve as the molecular electronic wires in the acceptor phase. Such compounds are expected to have a lower percolation threshold in the conjugated polymer/fullerene blend. Furthermore, linear fullerene arrays could make the transport 'road' to the electrode shorter and enhance the inter-fullerene electron hopping probability (the principle of a 'molecular electronic highway').

We first prepared dimeric fullerene structures, in which two fullerene moieties are bound either covalently or, more recently, in a supramolecular way through two self-complementary quadruple hydrogen bonding units.[20,21] In the course of the synthesis of the covalently bound fullerene dimer, in which the two fullerene units can freely have conformations in which the two fullerene units are in Van der Waals contact, we have recently discovered that two [60]fullerene units of a bis-methanofullerene, tethered by a *m*-phenylene bridge can dimerize photochemically through a [2+2]cycloaddition reaction of two parallel oriented C=C double bonds of the respective cages.[20] The reaction is depicted in Figure 2. This dimerization process is photochemically reversible, leading to steady state mixtures of monomeric and dimeric material
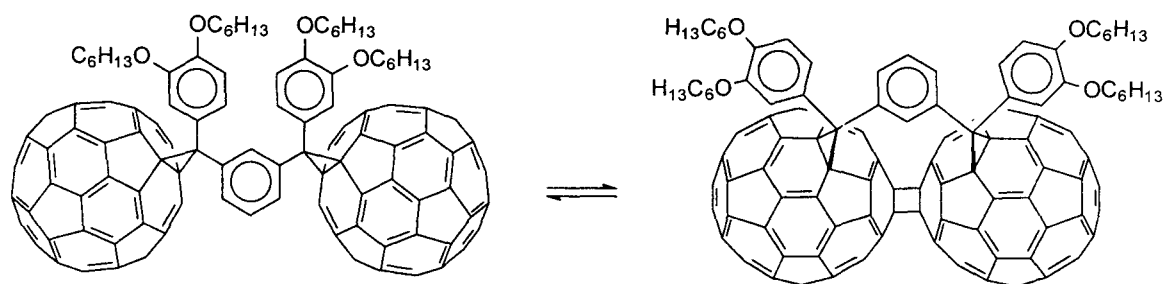
Figure 2. Photochemical inter-fullerene [2+2] cycloaddition and cycloreversion.

upon prolonged irradiation. Full recovery of the starting material (i.e. complete cycloreversion) was obtained upon heating the material above 100 °C.

These results add clear proof to long-standing proposals on structures and mechanisms involved in solid state photo- and pressure-polymerized C_{60}. Since [2+2] cycloaddition will ultimately influence the performance of devices in which the fullerene phase plays a role as electron-accepting/transporting medium, the presence of parallel oriented C=C bonds in the contact area between adjacent C_{60} moieties has to be taken into account in the design of fullerene arrays. Furthermore, it cannot be excluded that in a PPV/PCBM blend, such dimerization processes could take place in a more random way between neighboring PCBM molecules.

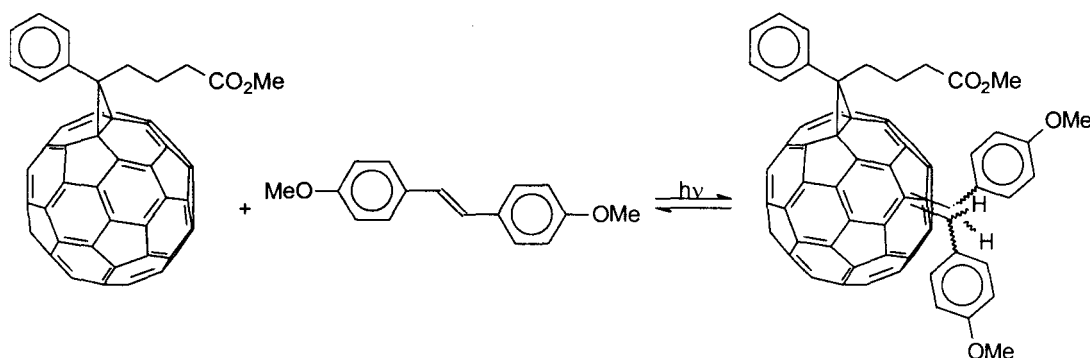## 3.2 Photochemical [2+2] cycloaddition reactivity of [60]fullerene and PCBM with selected alkenes

Several examples of [2+2] cycloaddition reactions between C_{60} and alkenes have been described in the literature.[22] In most cases, the reaction was carried out photochemically. Orfanopoulus *et al.* reported the cycloaddition between C_{60} and 4-methoxystyrene in presence of light.[23] Studies carried out with deuterated olefins demonstrated that the mechanism of cycloaddition process was not concerted. Intermediate formation of biradical or charged species was found. The observed formation of *cis* and *trans* isomeric products is in accord with such a mechanism. [2+2] cycloaddition reactions of C_{60} with stilbenes (as shortest model compounds for oligo- and poly (p-phenylene vinylene)s), conjugated oligomers, or -polymers have not been reported, yet. We have recently performed some experiments in order to determine whether such kind of reactions could play a role in 'anaerobic' degradation of plastic solar cells, especially the ones made of conjugated oligomer-fullerene dyads.

First, we investigated the reactivity of C_{60} with 4,4'-dimethoxystilbene using a 150 W sodium lamp as the light source. Since a possible [2+2] cycloaddition reaction is expected to pass through the C_{60} triplet excited state, the reaction mixtures were carefully degassed before irradiation. After 24 h of irradiation of a 1:20 molar ratio mixture in o-dichlorobenzene (ODCB), work-up gave a mixture of cis and trans [2+2] cycloadducts in 43% yield (Figure 3). The ^{1}H NMR in CDCl$_3$/CS$_2$ revealed a cis/trans ratio of 1/7, in accord with a biradical or dipolar mechanism.

cis + trans isomers (43 %)
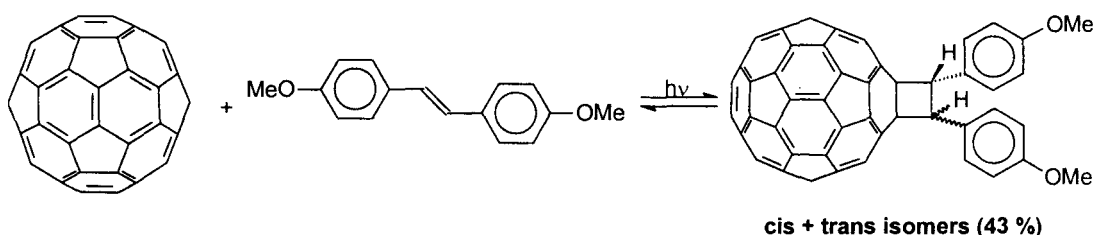
Figure 3. Reversible photochemical [2+2] cycloaddition of C_{60} and an electron rich stilbene.

While photochemical [2+2] cycloaddition reactions of C_{60} are commonly performed using a large excess of the alkene, we found that the yield of the reaction did not diminish dramatically upon irradiation of an equimolar molar solution.


Figure 4. Photochemical [2+2] cycloaddition of PCBM and 4,4'-dimethoxystilbene.

When pure cycloadduct was irradiated under the same conditions (concentration and reaction time), HPLC analysis of the product mixture revealed the presence of C_{60}. We therefore conclude that the photochemical process is reversible.

Next, this reaction was carried out with PCBM instead of C_{60}. In this case, a complex mixture of both regio- and stereoisomeric products is to be expected upon reaction with 4,4'-dimethoxystilbene, since methanofullerenes in general show regioselective reactivity only to a certain extent.[24] When the reaction was carried out under the same experimental conditions of concentration and time of irradiation as was used for C_{60}, HPLC /UV-Vis analysis of the reaction mixture indeed revealed the presence of fullerene bisadducts as a complex mixture of isomers (Figure 4). Hence, PCBM can also undergo this type of [2+2] cycloaddition. Solutions of pure PCBM in ODCB are photochemically stable in the absence of oxygen.

Alkoxy-substituted oligo(p-phenylene vinylene)s (OPVs) serve as much closer model systems for MDMO-PPV or poly [2-methoxy-5-(2-ethylhexyloxy)-*p*-phenylene vinylene] (MEH-PPV) than 4,4'-dimethoxystilbene. The photochemical reactivity of C_{60} with two different OPVs, OPV2 and OPV4,[25] was investigated using a 1/1 molar ratio in ODCB (Figure 5).

n = 1, 2
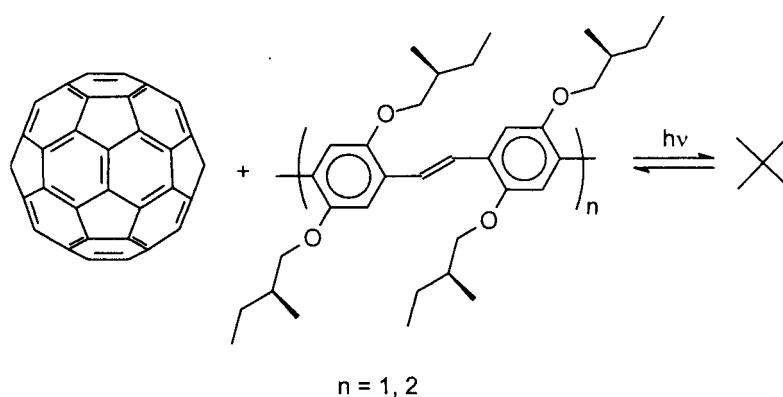
Figure 5. [60]Fullerene and two oligo(p-phenylene vinylene)s OPV2 (n=1) and OPV4 (n=2).

In both cases, no C_{60} derivatives were observed by HPLC/UV-Vis and thin layer chromatography (TLC) analysis of the product mixture. C_{60} was recovered in 98% instead. However, TLC analysis of the OPV4/C_{60} reaction mixture revealed the presence of a new and strongly blue fluorescent compound. Further work is necessary to prove that this may be the product of [2+2] homodimerization of the oligomer.[26] To explain the fact that a 4,4'-bisalkoxystilbene showed [2+2] cycloaddition with C_{60} and the OPVs (especially the quite similar OPV2!) did not, differences in both electronic and steric factors may have to be considered. These factors can be quite subtle. Therefore, a possible (minor) photochemical reactivity of (methano)fullerenes with (less conjugated, e.g. close to defect parts of) p-type PPV polymers cannot be predicted from these results.

Oligo- and polythiophene derivatives have also been used in plastic solar cell research. Cycloaddition reactions between C_{60} and (oligo) thiophenes are unknown. Since all π-electrons in oligothiophenes are part of aromatic rings, lowered reactivity towards cycloaddition is expected. However, a few examples of a photochemical reaction between thiophene derivatives and other olefins have been reported.[27]
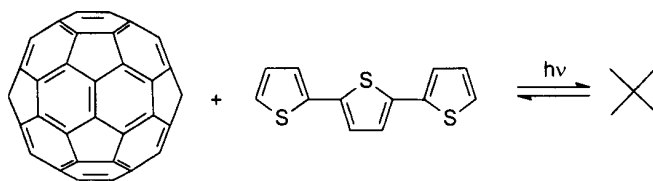
Figure 6. [60]fullerene and terthiophene.

Terthiophene (T3) serves as our shortest oligomer model system for polythiophenes. Therefore, we tested the photochemical stability of a 1/1 mixture of T3 and C_{60} in ODCB under the same experimental conditions as were used in the

above-mentioned experiments (Figure 6). No C_{60}-derivatives were observed neither by HPLC /UV-Vis nor TLC analysis. These studies will be extended to more electron rich oligothiophenes.

4. CONCLUSIONS

A number of chemical factors that may play a role in the degradation of plastic solar cells were discussed. This first and general study was done with special emphasis on the conjugated polymer/methanofullerene bulk-heterojunction type cells and the active layer thereof. We have shown that methanofullerenes and certain model compounds can undergo photochemical [2+2] cycloaddition reactions in the absence of oxygen or moisture. Analogous photochemical degradation processes could, in principle, also take place in the solar cells. However, *a priori* extrapolation of results obtained with model compounds that have only fragments of the extended π-electron systems of the ones applied in solar cells (e.g. a stilbene versus a PPV) is not possible. Furthermore, conjugated polymer degradation in solar cells may also take place at or close to chain defects rather than in the perfect regions. The exact chemical structure of such defects would have to be known to allow for investigation of the chemistry involved in this kind of degradation.

We hope that the considerations presented in this contribution may be of help to workers in the field with respect to the choice and design of materials and with respect to the design of the device architecture of organic (plastic) photovoltaic cells.

ACKNOWLEDGMENTS

REFERENCES

1. (a) N. S. Sariciftci, L. Smilowitz, A. J. Heeger, F. Wudl, "Photoinduced electron transfer from a conducting polymer to buckminsterfullerene", *Science* **258,** pp. 1474-1476, 1992; b) G. Yu, K. Pakbaz, A. J. Heeger, "Semiconducting Polymer diodes: Large size, low cost photodetectors with excellent visible-ultraviolet sensitivity", *Appl. Phys. Lett.,* **64**, pp. 3422-3424, 1994.

2. (a) G. Yu, A. J. Heeger, "Charge separation and photovoltaic conversion in polymer composites with internal donor-acceptor heterojunctions", *J. Appl. Phys.* **78**, pp. 4510-4515, 1995; (b) G. Yu, J. Gao, J. C. Hummelen, F. Wudl, A. J. Heeger, "Polymer Photovoltaic Cells: Enhanced Efficiencies via a Network of Internal Donor-Acceptor Heterojunctions", *Science* **270**, pp. 1789-1791, 1995; (c) J. J. M. Halls, C. A. Walsh, N. C. Greenham, E. A. Marseglia, R. H. Friend, S. C. Moratti, A. B. Holmes, "Efficient photodiodes from interpenetrating polymer networks", *Nature,* 376, pp. 498-500, 1995; (d) D. Gebeyehu, F. Padinger, C. J. Brabec, T. Fromherz, J. C. Hummelen, N. S. Sariciftci, "Characterization of large area flexible plastic solar cells based on conjugated polymer/fullerene composites", *Int. J. Photoenergy,* **1**, pp. 89-93, 1999; (e) T. Fromherz, F. Padinger, D. Gebeyehu, C. Brabec, J. C. Hummelen, N. S. Sariciftci, "Comparison of photovoltaic devices containing various blends of polymer and fullerene derivatives", *Sol. Energy Mat. Sol. Cells* **63**, pp. 61-68, 2000.

3. S. E. Shaheen, C. J. Brabec, F. Padinger, T. Fromherz, J. C. Hummelen, N. S. Sariciftci, "Enhanced efficiency bulk-heterojunction plastic solar cells", *Appl. Phys. Lett.* In print

4. J.-F. Nierengarten, J.-F. Eckert, J.-F Nicoud, L. Ouali, V. Krasnikov, G. Hadziioannou, "Synthesis of a C_{60}-oligophenylenevinylene hybrid and its incorporation in a photovoltaic device", Chem. Comm. Pp. 617-618, 1999.

5. E. Peeters, P.A. van Hal, J. Knol, C.J. Brabec, N. S. Sariciftci, J.C. Hummelen, R.A. J. Janssen, "Synthesis, Photophysical Properties and Photovoltaic Devices of Oligo(p-Phenylene Vinylene)-Fullerene Dyads", *J. Phys. Chem B*, **104**, pp. 10174-90, 2000.

6. (a) A.M. Marcos Ramos, M.T. Rispens, J.C. Hummelen, R.A.J. Janssen, "A poly(p-phenylene ethynylene vinylene) with pendant fullerenes", presented at ICSM2000, Gastein, Austria, July 15-21, 2000; submitted to *Synth. Metals.* (b) O. Inganäs *et al.*, presented at ICSM2000, Gastein, Austria, July 15-21, 2000.

7. S.C. Veenstra, U. Stalmach, V.V. Krasnikov, G. Hadziioannou, H.T. Jonkman, A. Heeres, G.A. Sawatzky, "Electronic transport and semiconductors- Energy level alignment at the conjugated phenylenevinylene oligomer-metal Interface", *Appl. Phys. Lett.* **76**, pp. 2253-2255, 2000.

8. L.S. Hung, C.W. Tang, M.G. Mason, "Enhanced electron injection in organic electroluminescence devices using an Al/LiF electrode", *Appl. Phys. Lett.* **70**, pp. 152-154, 1997.

9. G. E. Jabbour, Y. Kawabe, S.E. Shaheen, J.F. Wang, M.M. Morrell, B. Kippelen, N. Peyghambarian, "Highly efficient and bright organic electroluminescent devices with an aluminum cathode", *Appl. Phys. Lett.* **71**, pp. 1762-1764, 1997.

10. W.R. Salaneck, J.-L. Brédas, "The Metal-on-Polymer Interface in Polymer Light Emitting Diodes", *Adv. Mater.* **8**, pp. 48-52, 1996.

11. MDMO-PPV: poly [2-methoxy-5-(3',7'-dimethyloctyloxy)-*p*-phenylene vinylene]; PCBM: [6,6] phenyl C_{61}-butyric acid methyl ester (see J.C. Hummelen, B.W. Knight, F. LePeq, F. Wudl, J. Yao, C.L. Wilkins, "Preparation and characterization of fulleroid and methanofullerene derivatives", *J. Org. Chem.* **60**, pp. 532-538, 1995)

12. L.C. Chen, D. Godovsky, O. Inganäs, J.C. Hummelen, R.A.J. Janssen, M.R. Andersson, "Polymer solar cells from stratified multilayers of donor-acceptor blends", *Advanced Materials* **12**, pp.1367-70, 2000.

13. (a) H. Neugebauer, C.J. Brabec, J.C. Hummelen, R.A.J. Janssen, N.S. Sariciftci, "Stability Studies and Degradation Analysis of Plastic Solar Cell Materials by FTIR Spectroscopy", *Synth. Metals* **102**, pp. 1002-1003, 1999; (b) H. Neugebauer, C. Brabec, J.C. Hummelen, N.S. Sariciftci, "Stability and photodegradation mechanisms of conjugated polymer/fullerene plastic solar cells", *Sol. Energy. Mat. Sol. Cells* **61**, pp. 35-42, 2000.

14. K.M. Creegan, J.L. Robbins, W.K. Robbins, J.M. Millar, R.D. Sherwood, P.J. Tindall, D.M. Cox, A.B. Smith III, J.P. McCauley Jr., D.R. Jones, R.T. Gallagher, "Synthesis and characterization of $C_{60}O$, the first fullerene epoxide", *J. Am. Chem. Soc.* **114**, 1103-1107, 1992.

15. C. Taliani, G. Ruani, R. Zamboni, R. Danieli, S. Rossini, V.N. Denisov, V.M. Burlakov, F. Negri, G. Orlandi, F. Zerbetto, "Light-induced oxygen incision of C_{60}", *J. Chem.Soc.Chem.Commun.* pp. 220-221, 1993

16. J.W. Arbogast, A.P. Darmanyan, C.S. Foote, Y. Rubin, F.N. Diederich, M.M. Alvarez, S.J. Anz, R.L. Whetten, "Photophysical properties of C_{60}", *J. Phys. Chem.* **95**, pp. 11-12, 1991

17. T. Konishi, M. Fujitsuka, O. Ito, "Evaluation of rate constant for electron transfer from C_{60}^{-} anion radical to molecular oxygen by laser flash photolysis method", *Chem. Lett.* pp. 202-203, 2000.

18. (a) M.G. Hill, K.R. Mann, L.L. Miller, J.-F. Penneau, "Oligothiophene Cation Radical dimers: An alternative To Bipolarons in Oxidized Polythiophene", *J. Am. Chem. Soc.* **114**, pp. 2728-2730, 1992; (b) P. Audebert, P.Hapiot, J.-M. Pernaut, P.Garcia, "Electrochemical reactivity of the oxidized species of thiophene oligomers. Formal oxidation potential of α-bromo-α'-methoxy-quaterthienyl", *J. Electroanal. Chem.* **361**, pp. 283-288, 1993; (c) P. Bäuerle, U. Segelbacher, A. Maier, M. Mehring, "Electronic Structure of Mono- and Dimeric Cation Radicals in End-Capped Oligothiophenes", *J. Am. Chem. Soc.* **115**, pp. 10217-10223, 1993; (d) J.A.E.H. van Haare, L. Groenendaal, E.E. Havinga, R.A.J. Janssen, E.W. Meijer, "π-Dimers of End-Capped Oligopyrrole Cation Radicals", *Angew. Chem. Int. Ed. Engl.* 35, pp. 638-639, 1996; (e) A. Sakamoto, Y. Furukawa, M. Tasumi, "Spectroscopic Studies on the Radical-Cation Dimer of a Model Compound of Poly(p-phenylenevinylene). Similarities between the Dimer and the State of Positive Polarons in the Sulfuric-Acid-Treated Polymer", *J. Phys. Chem. B* **101**, pp. 1726-1732, 1997; (f) E. Levillain, J. Roncali, "Structural Control of the Reversible Dimerization of π-Conjugated Oligomeric Cation Radicals", *J. Am. Chem. Soc.* **121**, pp. 8760-8765, 1999.

19. J.J. Apperloo, B.M.W. Langeveld-Voss, J. Knol, J.C. Hummelen, R.A.J. Janssen, "Unexpected Dimerization of Oxidized Fullerene-Oligothiophene-Fullerene Triads", *Advanced Materials* **12**, pp. 908-911, 2000

20. J. Knol, J.C. Hummelen, "Photodimerization of a m-phenylenebis(arylmethanofullerene): The first rigorous proof for photochemical inter-fullerene [2+2] cycloaddition", *J. Am. Chem. Soc.* **122**, pp. 3226-3227, 2000.

21. M.T. Rispens, L. Sánchez, J. Knol, J.C. Hummelen, "Supramolecular organization of fullerenes by quadruple hydrogen bonding", submitted for publication.

22. (a) S.R. Wilson, N. Kaprinidis, Y. Wu, D.I. Schuster, "A new reaction of fullerenes: [2+2] photocycloadditions of enones", *J. Am. Chem. Soc.* **115**, 8495-8496, 1993; (b) X. Zhang, A. Romero, C.S. Foote, "Photochemical [2+2]cycloaddition of N,N'-diethylpropynylamine to C_{60}", *J. Am. Chem. Soc.* **115**, 11024-11025, 1993.(c) S.R. Wilson, Y. Wu, N. Kaprinidis, D.I. Schuster, C.J. Welch, "Resolution of enantiomers of cis-and trans-fused C_{60}-enone [2+2]photoadducts", *J. Org. Chem.* **58**, 6548-6549, 1993; (d) X. Zhang, C.S. Foote, "[2+2]Cycloadditions of fullerenes: synthesis and characterization of $C_{62}O_3$ and $C_{72}O_3$, the first fullerene anhydrides", *J. Am. Chem. Soc.* **117**, 4271-4275, 1995; (e) D.I. Schuster, J. Cao, N. Kaprinidis, Y. Wu, A.W. Jensen, Q. Lu, H. Wang, S.R. Wilson, "[2+2]Cycloaddition of cyclic enones to C_{60}", *J. Am. Chem. Soc.* **118**, 5639-5647, 1996; (f) X. Zhang, A. Fan, C.S. Foote, "[2+2]Cycloadditions of fullerenes with electron-rich alkenes and alkynes", *J. Org. Chem.* **61**, 5456-5461, 1996; (g)

A.W. Jensen, A. Khong, M. Saunders, S.R. Wilson, D.I. Schuster, "Photocycloaddition of cyclic 1,3-diones to C_{60}", *J. Am. Chem. Soc.* **119**, 7303-7307, 1997; (h) G. Vassilikogiannakis, N. Cronakis, M. Orfanopuolus, "A New [2+2] functionalization of C_{60} with alkyl-substituted 1,3-butadienes: a mechanistic approach. stereochemistry and isotope effects", *J. Am. Chem. Soc.* **120**, 9911-9920, 1998; (i) G. Vassilikogiannakis, M. Orfanopuolus, 'Regio and stereoselectivity of the [2+2]photocycloaddition of acyclic enones to C_{60}", *J. Org. Chem.* **64**, 3392-3393, 1999.

23. (a) G. Vassilikogiannakis, M. Orfanopoulos, "Stereochemistry and Isotope Effects of the [2+2]Cycloadditions of arylalkenes to C_{60}. A stepwise mechanism", *J. Am. Chem. Soc.* **119**, pp. 7394-7395, 1997; (b) G. Vassilikogiannakis, M. Orfanopoulos, "[2+2]Cycloadditions of cis/trans-4-propenylanisole to C_{60}", *Tetrahedron Lett.* **38**, pp. 4323-4326, 1997.

24. A. Hirsch, I. Lamparth, H.R. Karfunkel, "Fullerene chemistry in three dimensions: isolation of seven regioisomeric bisadducts and chiral trisadducts of C_{60} and di(ethoxycarbonyl)methylene", *Angew. Chem. Intl. Ed. Engl.* **33**, 437-438, 1994.

25. E. Peeters, R.A. J. Janssen, S.C.J. Meskers, E.W. Meijer, "Optical activity of chiral π-conjugated oligomers and polymers", *Polym. Prep.* **40,** pp. 519-520, 1999.

26. Note: Irradiation of a mixture of C_{60} and OPV4 in toluene with a 600nm laser, however, slowly lead to the formation of fullerene derivatives as determined by HPLC-UV-Vis analysis of the product mixture (P.v.Hal, R.A.J. Janssen, private communication)

27. (a) D.C. Neckers, F.L. Wagenaar, "Synthesis of 3,4-benzo-2-thiabicyclo[3.2.0]hepta-1,3-diene", *J. Org. Chem.* **46**, pp. 3939-3940, 1981; (b) D.C. Neckers, F.L. Wagenaar, D. Hauenstein, R.A. Jacobson, "Photochemical cycloadditions of 2,3-dihalobenzo[b[thiophenes: stereochemical and mechanistic results", *J. Org. Chem.* **48**, pp. 1725-1732, 1983; (c) M. Ikeda, T. Uno, K.I. Homma, K. Ohno, Y. Tamura, "Beckman fission of some fused cyclobutanones: a new entry into indole-2-acetonitriles and benzo[b]thiophene-2-acetonitrile", *Synth. Commun.* **10**, pp. 437-450, 1980