



Stability and photodegradation mechanisms of conjugated polymer/fullerene plastic solar cells

H. Neugebauer^{a,*}, C. Brabec^a, J.C. Hummelen^b, N.S. Sariciftci^a

^aPhysical Chemistry, Johannes Kepler University of Linz, Altenbergerstraße 69, A-4040 Linz, Austria

^bOrganic and Molecular Inorganic Chemistry, University of Groningen, Nijenborgh 4, 9747 AG Groningen, Netherlands

Abstract

Degradation studies of poly(2-methoxy-5-(3',7'-dimethyloctyloxy)-1,4-phenylene-vinylene) (MDMO-PPV), fullerenes ((6,6)-phenyl C₆₁-butyric acid methyl ester (PCBM) and C₆₀), and mixtures, which are the photoactive components in plastic solar cells, are shown. The degradation processes of the individual components and of a 1:3 mixture are characterized by attenuated total reflection Fourier transform infrared (ATR-FTIR) spectroscopy and by current/voltage (*I*-*V*) measurements of devices under the influence of light and oxygen. A faster degradation rate was found for the polymer compared with C₆₀. In composites with fullerenes, the stability of MDMO-PPV is enhanced due to the fast electron transfer to C₆₀. © 2000 Elsevier Science B.V. All rights reserved.

Keywords: Plastic solar cells; Degradation; Infrared spectroscopy; *I*-*V* Measurements

1. Introduction

A tremendous research effort was devoted to the development of photovoltaic cells in the last decades. Besides the improvement of inorganic photovoltaic systems, a lot of effort has been put in the development of organic semiconductor devices, because the latter offer the advantages of low cost and facile processing for large area production [1–3]. Especially the flexibility of chemical tailoring of desired properties, as well as the cheap technology already well developed for all kinds of plastic thin film applications promise potential for large scale photovoltaic device production based

* Corresponding author. Tel.: 0043-732-2468766; fax: 0043-732-2468770.

E-mail address: helmut.neugebauer@jk.uni-linz.ac.at (H. Neugebauer)

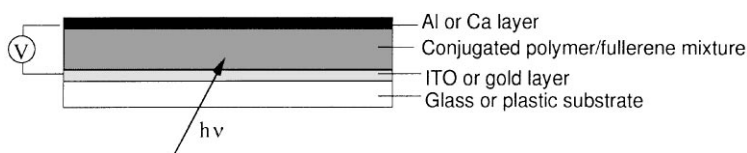


Fig. 1. Device structure of plastic solar cells.

on polymers. The mechanical flexibility of plastic materials is welcome for all photovoltaic applications onto curved surfaces in indoor and outdoor applications.

Organic materials for use in photovoltaic devices require a good chemical stability and high optical absorption in the visible range with respect to the AM 1.5 spectrum. Efficiencies of the first polymeric solar cells, based on hole conducting conjugated polymers (mainly polyacetylene) were rather discouraging [4]. Encouraging breakthrough to higher efficiencies was achieved by switching to different classes of electron-donor-type conjugated polymers (polythiophenes (PT), polyphenylenevinylenes (PPV) and their derivatives) and by mixing them with suitable electron acceptors like fullerenes [5–9]. Prototypes of photovoltaic devices based on a polymeric donor/acceptor network showed scattered values for solar energy conversion efficiencies of around 1–3% obtained under different conditions [10–12]. Especially the photovoltaic properties and the photophysics of conjugated polymer/fullerene solid composites have been well investigated in the last years [13].

Plastic solar cells consist of an electron donor and an electron acceptor material, which can be either arranged in a bilayer structure or in an interpenetrating network. As electrodes, a transparent gold or ITO film on glass or plastic substrate on one side and an evaporated Al or Ca layer on the other side are used. The device structure is shown in Fig. 1.

Apart from the necessity for efficiency improvement, stability is another problem for all the applications of conjugated polymers. Especially under the influence of light and by simultaneous exposure to oxygen, a rapid degradation occurs. Protection from air and humidity is absolutely necessary to achieve long lifetimes [14].

In the development stage of plastic solar cells, where a number of different compounds have to be characterized, a fast and reliable testing procedure for stability has to be applied. In this paper, we show controlled degradation experiments performed with the individual components and with the actual mixture as used in plastic solar cells [15]. The degradation is studied using attenuated total reflection fourier transform infrared (ATR-FTIR) spectroscopy and by the determination of current/voltage characteristics (I - V measurements) of the devices.

2. Experimental

As electron donor, we used poly(2-methoxy-5-(3',7'-dimethyloctyloxy)-1,4-phenylenevinylene) (MDMO-PPV), prepared as reported in the literature [16,17]. Electron acceptor substances were (6,6)-phenyl C_{61} -butyric acid methyl ester

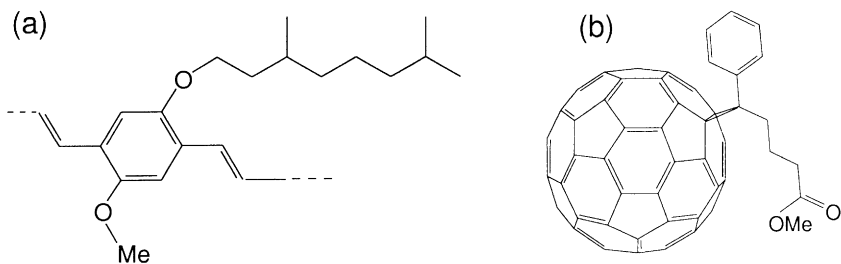


Fig. 2. Structure of the substances. (a) MDMO-PPV, (b) PCBM.

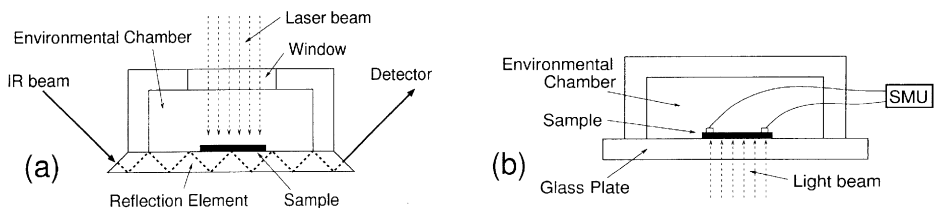


Fig. 3. (a) Setup for ATR-FTIR spectroscopy. (b) Setup for I - V measurements.

(PCBM)[18] and C_{60} (MER Corp.). The structures of the substances is shown in Fig. 2. For solar cell devices, a mixture of MDMO-PPV : C_{60} 1 : 3 was used.

ATR-FTIR spectra were measured using a FTIR Spectrometer BRUKER IFS66S with a DTGS detector. Thin film samples were dropcasted from *o*-dichlorobenzene (ODCB) solution on the surface of a ZnSe ATR reflection element and dried under vacuum. The substrates were mounted in an environmental cell, which allows the recording of ATR spectra simultaneously with the illumination of the sample by laser light in a defined atmosphere. FTIR spectra with a measurement time of 5 min were recorded consecutively during a period of about 8 h. For illumination, we used an argon ion laser (Coherent Innova 400) at 488 nm and an illumination of 30 mW/cm^2 on the sample. The setup for ATR-FTIR measurements is shown in Fig. 3(a).

Current/voltage curves were recorded with a Keithley SMU 2400 unit. During these measurements, the sample was illuminated using a white light source with 10 mW/cm^2 . The setup for I - V measurements is shown in Fig. 3(b).

3. Results and discussion

3.1. ATR-FTIR degradation studies

In order to get a fast characterization of the degradation processes, the individual components (MDMO-PPV and C_{60}) as well as the 1 : 3 mixture as used in plastic solar cells, were studied under illumination in pure oxygen. ATR-FTIR spectra before

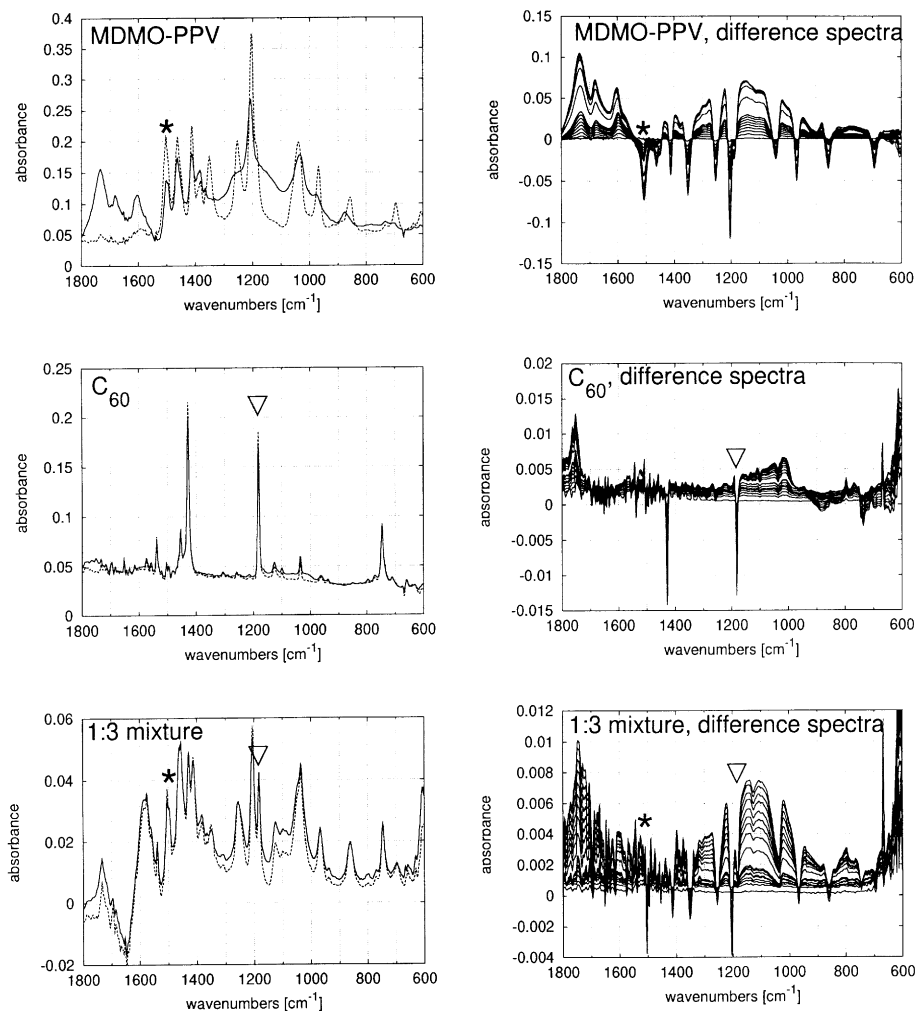


Fig. 4. FTIR spectra of degradation in oxygen. Left column, dashed lines: before degradation, solid lines: after degradation (reference spectra: reflection element without sample). Right column: difference spectra during degradation (reference spectra at the beginning of the degradation process). (*) 1506 cm^{-1} band of MDMO-PPV, (∇) 1182 cm^{-1} band of C_{60} .

and after a 8 h degradation process as well as difference spectra showing only the spectral changes during degradation, are presented in Fig. 4 for MDMO-PPV, C_{60} and the 1 : 3 mixture.

The characterization of the degradation process was performed by analysis of the time dependence of the decay of specific absorption bands at 1506 cm^{-1} (MDMO-PPV) and 1182 cm^{-1} (C_{60}) using spectral fitting techniques. The results are shown in Fig. 5.

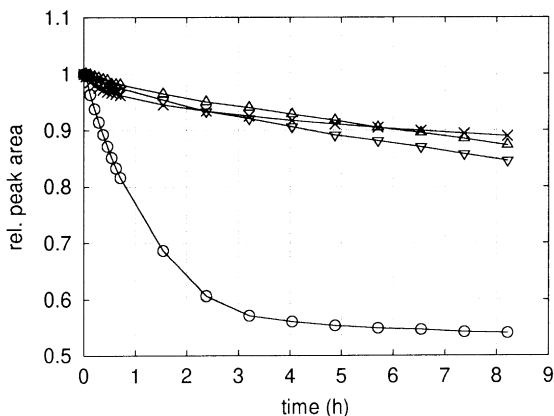


Fig. 5. Time dependence of specific absorption bands. (○) MDMO-PPV 1506 cm^{-1} , (×) C_{60} 1182 cm^{-1} , (△) mixture 1506 cm^{-1} , (▽) mixture 1182 cm^{-1} .

For the individual components, the degradation in oxygen atmosphere occurs much faster for MDMO-PPV compared to C_{60} or PCBM (not shown in Figs. 4 and 5). For long-term applications, especially the stability of the polymeric electron donor in the mixture for solar cells has to be improved. As has been shown in a previous paper, the degradation of MDMO-PPV can be diminished to a very low degree by performing the stability test in argon atmosphere [14].

However, in the mixture the degradation of MDMO-PPV is much slower compared to the pure polymer sample. The fast electron transfer from the polymer to C_{60} after excitation accompanied by the formation of positive charged polarons on the chain decreases strongly the reactivity of the polymer against oxygen, probably by quenching the triplet formation on the polymer and avoiding a triplet-triplet annihilation reaction with oxygen under formation of reactive singlet oxygen [19,20]. As degradation products, carbonylic structures with characteristic absorption bands between 1600 and 1800 cm^{-1} [21] can be seen (right column of Fig. 4). Aromatic (absorption between 1600 and 1700 cm^{-1}) as well as aliphatic ketones (absorption above 1700 cm^{-1}) with additional weaker absorption around 1000 – 1200 cm^{-1} occur [22].

3.2. *I-V* degradation measurements

Photovoltaic devices were produced from a toluene solution containing MDMO-PPV:PCBM 1:3 by a doctor blade technique, giving homogeneous films with typical thickness between 100 and 200 nm under ambient conditions. After transferring the cells into an argon glove box, the *I-V* characteristics were monitored for several days. Continuous *I-V* sweeps between $+2$ and -2 V in the dark and under white light illumination with 10 mW/cm^2 showed no significant performance decrease. In order to test the performance under ambient conditions, the cells were removed from the glove box and characterized in oxygen environment by similar *I-V*

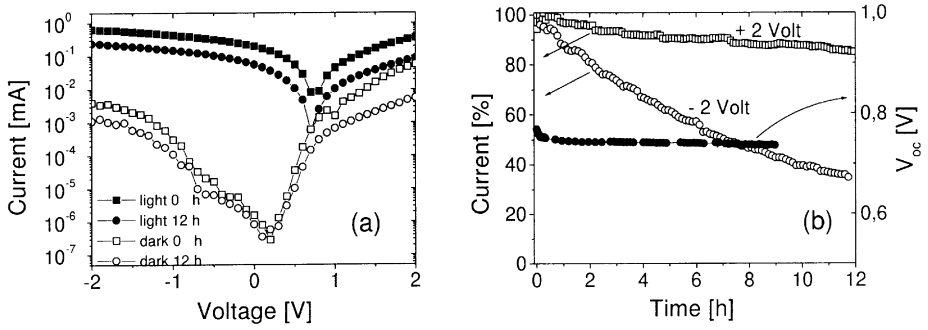


Fig. 6. (a) I - V curve (dark and illuminated) of an unprotected 4 cm^2 device before and after 12 h of continuous I - V sweeps from -2 to 2 V in pure oxygen. The overall power conversion efficiency under white light is 0.25% . (b) Degradation of photocurrent under constant bias and of V_{oc} within 12 h.

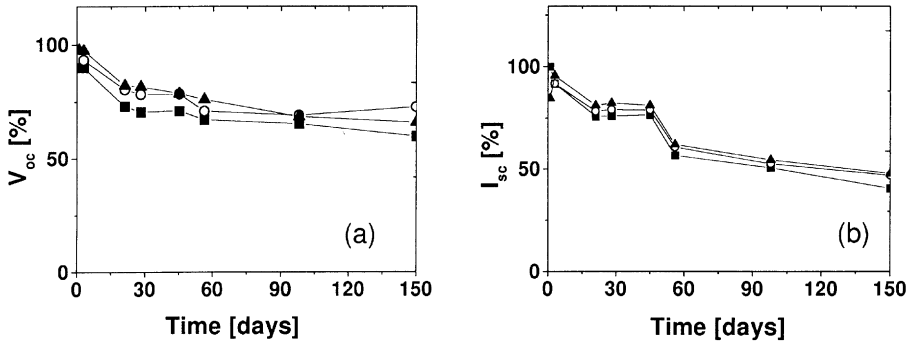


Fig. 7. Shelf life time of protected cells.

studies. Fig. 6 shows the changes of the I - V characteristics of a cell during 12 h test run in oxygen.

After 12 h the short-circuit current (I_{sc}) as well as the photocurrent under bias decreased by a factor of about three (Fig. 6(a)). In addition, a similar decrease of the dark current was observed. The kinetics of the degradation are influenced by the sign of the applied voltage (Fig. 6(b)). The observed faster photocurrent degradation for reverse bias (-2 V on the ITO electrode) may be due to the higher absolute value of the photocurrent under reverse bias compared to forward bias ($+2 \text{ V}$ on the ITO electrode), $|I_{ill}(-2 \text{ V})| > |I_{ill}(+2 \text{ V})|$, or to degradation processes under specific participation of the electrode materials (e.g. formation of insulating oxide layers). Under open-circuit conditions (with zero current flow), the photovoltage is found to be almost constant. Increased internal device resistivity upon photodegradation may be suggested, because the degradation does not influence, V_{oc} , but I_{sc} .

In Fig. 7 the long-term stability of protected plastic solar cells is monitored by V_{oc} and I_{sc} measurements. Cells have been produced under ambient room conditions

and sealed after application of the top electrode. No actions were taken to remove the residual oxygen from the cells, which may be adsorbed on the surface during production. The shelf life time of these devices is more than 150 d. The initial decrease of V_{oc} and I_{sc} can be due to the residual oxygen built in during production in air.

4. Conclusion

In this paper we present a fast and reliable method for testing the stability and for characterizing the degradation processes of individual components and their mixtures used for plastic solar cells. The analysis of the degradation kinetics shows that the high degradation rate of the conjugated polymer under influence of light and oxygen is significantly decreased when the polymer is mixed with fullerenes (as used in plastic solar cells). The stability of the conjugated polymer in a mixture, which forms a charge transfer donor and acceptor couple, is higher than the stability of single component devices, e.g. polymer light-emitting diodes, where the conjugated polymer was found to degrade within minutes under oxygen influence [23]. Also I - V curves confirm the better stability of solar cell mixtures compared to LEDs with a single polymeric component. We conclude that the stabilization effect of C_{60} is due to the fast electron transfer which empties the highly reactive excited state of the polymer.

In our experiments, the combination of light and oxygen always leads to a decrease in photocurrent. No initial increase, as observed for organic small molecule photo-diodes [24], was found. Our results indicate an increase of the overall serial resistivity by degradation.

Acknowledgements

This work was performed within the Christian Doppler Foundation's dedicated Laboratory for Plastic Solar Cells funded by the Austrian Ministry of Economic Affairs and Quantum Solar Energy Linz Ges.m.b.H.

The work is supported by the "Fonds zur Förderung der wissenschaftlichen Forschung" of Austria, Projects No. P11457-CHE and P-12680-CHE.

The authors gratefully acknowledge R.A.J. Janssen, Laboratory of Macromolecular and Organic Chemistry, Eindhoven University of Technology, for providing MDMO-PPV.

References

- [1] A.J. Heeger, P. Smith, in: J.L. Bredas, R. Silbey (Eds.), *Conjugated Polymers*, Kluwer, Dordrecht, 1991, p. 141.
- [2] J.L. Brédas, R.R. Chance, *Conjugated Polymeric Materials: Opportunities in Electronics*, in: *Optoelectronics and Molecular Electronics*, Kluwer, Dordrecht, 1990.
- [3] W.R. Salaneck, D.T. Clark, E.J. Samuelsen, in: *Science and Application of Conducting Polymers*, Adam Hilger, Bristol, 1991.

- [4] J. Kanicki, in: T.A. Skotheim (Ed.), *Handbook of Conducting Polymers*, Marcel Dekker, New York, 1986, p. 544.
- [5] N.S. Sariciftci, L. Smilowitz, A.J. Heeger, F. Wudl, *Science* 258 (1992) 1474.
- [6] L. Smilowitz, N.S. Sariciftci, R. Wu, C. Gettinger, A.J. Heeger, F. Wudl, *Phys. Rev. B* 47 (1993) 13835.
- [7] B. Kraabel, J.C. Hummelen, D. Vacar, D. Moses, N.S. Sariciftci, A.J. Heeger, F. Wudl, *J. Chem. Phys.* 104 (1996) 4267.
- [8] S. Morita, A.A. Zakhidov, K. Yoshino, *Solid State Commun.* 82 (1992) 249.
- [9] K. Yoshino, X.H. Yin, S. Morita, T. Kawai, A.A. Zakhidov, *Solid State Commun.* 85 (1993) 85.
- [10] G. Yu, J. Gao, J.C. Hummelen, F. Wudl, A.J. Heeger, *Science* 270 (1995) 1789.
- [11] J. Gao, F. Hide, H. Wang, *Synth. Met.* 84 (1997) 979.
- [12] M. Granström, K. Petritsch, A.C. Aries, A. Lux, M.R. Andersson, R.H. Friend, *Nature* 395 (1998) 257.
- [13] N.S. Sariciftci, A.J. Heeger, in: H.S. Nalwa (Ed.), *Handbook of Organic Conductive Molecules and Polymers*, Vol. 1, Wiley, Chichester, 1997, p. 413.
- [14] H. Neugebauer, C.J. Brabec, J.C. Hummelen, R.A.J. Janssen, N.S. Sariciftci, *Synth. Met.*, 102 (1999) 1002.
- [15] C.J. Brabec, F. Padinger, V. Dyakonov, J.C. Hummelen, R.A.J. Janssen, N.S. Sariciftci, in: H. Kuzmany, J. Fink, M. Mehring, S. Roth (Eds.), *AIP Conference Proceedings 442, Electronic Properties of Novel Materials — Progress in Molecular Nanostructures*, American Institute of Physics, Woodbury, New York, 1998, p. 519.
- [16] G.H. Gelinck, J.W. Warman, E.G.J. Staring, *J. Phys. Chem.* 100 (1996) 5485.
- [17] H. Spreitzer, W. Kreuder, H. Becker, H. Schoo, R. Demandt, PCT Patent Application WO 98/27136. 1996.
- [18] J.C. Hummelen, B.W. Wright, F. Lepec, F. Wudl, *J. Org. Chem.* 60 (1995) 532.
- [19] R.D. Scurlock, B. Wang, P.R. Ogilby, J.R. Sheats, R.L. Clough, *J. Am. Chem. Soc.* 117 (1995) 10194.
- [20] G.D. Hale, S.J. Oldenburg, N.J. Halas, *Appl. Phys. Lett.* 71 (1997) 1483.
- [21] G. Geuskens, C. David, in: G. Geuskens (Ed.), *Degradation and Stabilisation of Polymers*, Applied Science Publishers, London, 1975 (Chapter 6).
- [22] *The Aldrich Library of FTIR Spectra*, Edition II, Sigma Aldrich Co, Milwaukee, 1997.
- [23] A.J.F. Liedenbaum, J.J.M. Vleggaar, *Philips J. Res.* 51 (1998) 511.
- [24] J. Simon, J.J. Andre, *Molecular Semiconductors*, Springer, Berlin, 1985.