Significant Improvement of Polymer Solar Cell Stability[†]

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Received June 19, 2005
Revised Manuscript Received August 26, 2005

Solar cells based on polymers are a technology that may become a cheap renewable energy source. So far results have been promising as documented through many recent reports and detailed studies.[1−6] The conversion efficiencies that can be obtained for the best performing polymer-based solar cells are in the 2−5% range.[7−10] Common to all the efficient systems is the use of a conjugated polymer [i.e., polythiophene or poly(phenylene vinylene), PPV] with solubilizing side chains (i.e., linear or branched alkyl side chains) mixed with a large proportion of a soluble fullerene derivative (i.e., PCBM). The fullerene derivative most often constitutes a significant proportion of the active layer by weight. In the case of PPV/PCBM-based bulk heterojunctions a fullerene content of 80% (w/w) has been shown to be optimal.[11] There are several important goals that must be met before widespread application of polymer solar cells can be anticipated. The efficiency is most often considered because it is relatively easy to measure, and it is a figure that can be compared directly with existing technologies. The lifetime under illumination and upon storage in the dark, however, has been given relatively little attention. The lifetimes observed for polymer-based photovoltaics are very short compared to inorganic silicon-based solar cells with lifetimes in excess of 25 years. For polymer solar cells the lifetime is most often defined as the time it takes for the efficiency to reach half its initial or maximum value. The lifetimes that have been reported are very short when the devices are operated in the atmosphere, and typically the values are in the range of minutes to a few days.[12−19] Detailed reports on the mechanisms of polymer photovoltaic degradation have been relatively scarce in the literature. The first detailed reports by Neugebauer et al. made extensive use of bulk techniques such as infrared (IR) spectroscopy to monitor changes in molecular structure by following the intensity of certain IR absorption bands as a function of time.[12,13] Recent work by Jeranko et al. included two-dimensional mapping of the solar cell current using a laser.[17] This work showed many interesting features such as the preponderance of edge degradation, hot spots, and dead spots. Systematic studies on the influence of the device geometry on the degradation curves measured as the short circuit current versus time revealed that both atmosphere-dependent and atmosphere-independent mechanisms can be responsible for solar cell degradation.[18] Finally recent studies on polymer photovoltaic degradation using $^{18}O_2$ isotopic labeling combined with time-of-flight secondary ion mass spectrometry analysis and depth profiling established that several degradation mechanisms are in play simultaneously.[19] The most important reactions taking place are photoreduction of the conjugated polymer by reaction with the aluminum electrode, diffusion of the aluminum from the electrode into the active layer, and reaction with molecular oxygen throughout the cell. From a fundamental and technological point of view degradation is inevitable when subjecting an organic material to strong sunlight (UV−vis), elevated temperatures, electric currents, a reactive metal electrode, oxygen, and water. While the realization of infinitely stable polymer-based solar cells could seem like a futile exercise, it should be noted that a fundamental understanding of the degradation mechanisms could allow one to make better polymer materials that will extend the lifetime of photovoltaic devices. From a technological point of view an operating lifetime of 1000−10 000 h is sufficient for many products. From an experimental point of view it gets increasingly difficult to perform the measurements as the lifetimes increase beyond a few hundred hours corresponding to a good week of measurements. Typical sun simulator lamps are not stable over extended periods of time. Both the spectral distribution and the light power density changes during the lifetime of the light bulb, which is typically between 100 and 1000 h. For extended measurements on solar cells using sun simulation several light bulbs will have to be changed, and while careful calibration is required at each change comparison is still associated with some inaccuracy (we estimate 5−10%). One partial solution

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[†] A patent application covering this invention has been filed.

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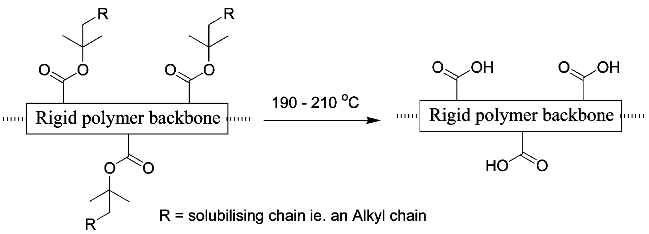
10.1021/cm051320q CCC: $30.25

Scheme 1



to this problem is accelerated lifetime testing that makes use of an empirical relationship between temperature and the speed of degradation. For a thermally activated process an increase in the temperature of the experiment leads to an increase in the rate of degradation. According to the excellent work by Schuller et al.[16] the acceleration factor for testing at 72 °C as compared to 25 °C is about 4. The exact numerical value for the acceleration factor is undoubtedly dependent on the material and the preponderant degradation mechanisms for the given material. One can, however, use the result of Schuller et al. as a rule of thumb. There have been no reports detailing how one might improve on the lifetime of organic photovoltaics, but there have been reports that give clues as to how one might achieve a longer lifetime. Yang et al. elegantly studied the morphological changes of the active layer for PPV/PCBM mixtures using electron microscopy and electron diffraction techniques.[20] Their main finding was that the thermal stability of the morphology was limited. These phenomena were especially pronounced above the glass transition temperature of the polymer material. The obvious answer to the problem would, thus, be to raise the glass transition temperature, and while possible, this is generally associated with much poorer film forming and solubility properties of the polymer material. The visionary work by Liu et al. presented the synthesis of a polythiophene with thermocleavable side groups for the purpose of anchoring and creating a better electronic contact between a conjugated polymer and anatase. Their study took advantage of the facile thermal cleavage of esters between a carboxylic acid and a tertiary alcohol at temperatures around 190−210 °C.[21]

If the tertiary alcohol is of a moderate chain length, solubility in common organic solvents is easily achieved. After thermal cleavage the rigid polymer backbone is left insoluble without the side chains (Scheme 1). The principle is, thus, that one can have the desirable solution processing advantages, and once the film has been formed, a thermal treatment allows for a conversion of the material into an insoluble rigid form (i.e., with a much higher glass transition temperature). In our laboratory we regularly test polymer materials in polymer photovoltaic geometries with a focus on the stability and lifetime of the photovoltaic devices under simulated sunlight, atmospheres, and temperatures.

The polymer material used in the report by Liu et al. quickly distinguished itself as significantly different from any of the other materials we have tested in that the devices were very stable as shown in Figure 1. There are some obvious shortcomings with this material from a photovoltaic device point of view.

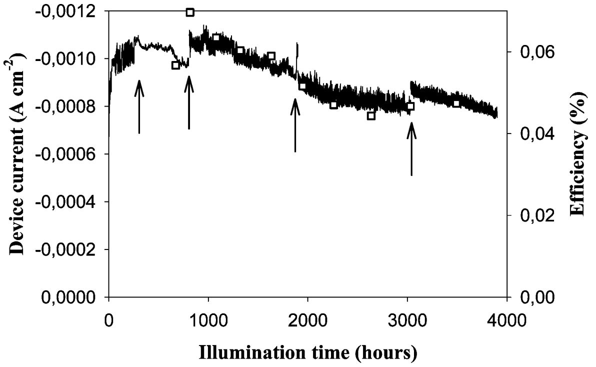
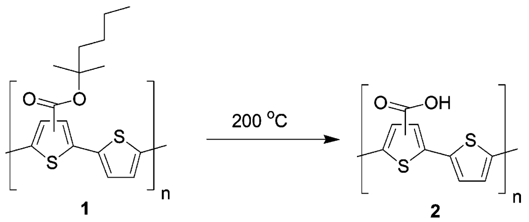


Figure 1. Lifetime (black curve, measured as the short circuit current every 10 s) and efficiency (squares) for a device based on **2** with a sublimed layer of C_{60} operated at a temperature of 72 ± 2 °C and a pressure of $<10^{-6}$ mbar under continuous sun simulation approaching AM1.5 spectral conditions with an incident intensity of 1000 W m^{-2}. The active area of the device was 3 cm^2. Arrows indicate light bulb changes and recalibration of the sun lamp with a bolometric pyranometer.

Scheme 2



The carboxylic acid function on every second thiophene ring was expected to react readily with reactive metal electrodes such as aluminum. We attempted many device geometries, and they all confirmed our expectations. Direct aluminum contact with **2** gave poor devices that might be due to reaction between aluminum and the carboxylic acid functionalities on the backbone (Scheme 2). A sublimed layer of C_{60} on top of the thermocleaved polymer film gave the desired stability. C_{60} has been reported to be a good barrier layer with aluminum electrodes.[18] The best efficiencies that could be obtained by this geometry is highly dependent on the thicknesses of the respective layers, whereby a maximum intensity of the electric field vector is ensured at the polymer−fullerene heterojunction interface as shown earlier.[22] Optimization in our experimental geometry where the active area is 10 cm^2 allowed us to reach a white light efficiency of 0.167% at 1000 W m^{-2} (AM1.5) as shown in Figure 2. While this figure for the efficiency is about 10−20 times lower than the best reports, our devices exhibited a very high degree of stability. A smaller active area could improve a little on the efficiency and the dark rectification ratio as this reduces the likelihood of film defects and resistive losses due to the sheet resistance (see Supporting Information). We have, however, employed realistic active areas of the devices (i.e., significantly more than 1 cm^2). The efficiency can most likely be improved by employing the concept of thermocleavable side groups while altering the thermocleavage mechanism such that different functional

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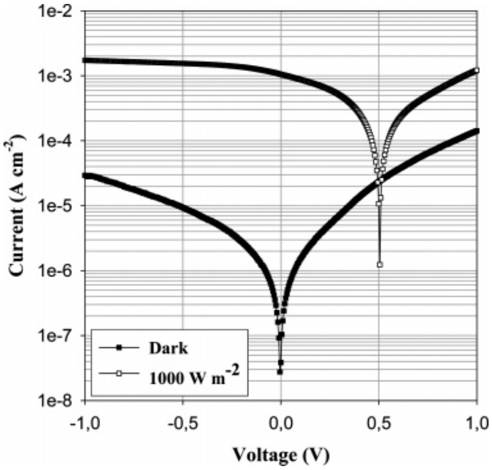

Figure 2. *IV* curves of an encapsulated device having an active area of 10 cm^2. Illumination was at 1000 W m^{-2} (AM1.5), and measurements were carried out at 72 °C. The device had values of $V_{oc} = 0.505$ V, $I_{sc} = 1.05$ mA cm^{-2}, FF = 29%, rectification @ |1 V| = 5, and efficiency = 0.167%. The device was prepared on a glass substrate with indium tin oxide (ITO) as the transparent oxide (10 Ω square^{-1}). The cleaved polymer film had an absorbance of 0.378 at λ_{max} (501 nm) and had a sublimed layer of C_{60} (50 nm) on top and a thermally evaporated aluminum electrode (0.2 Ω square^{-1}) to complete the device. The device was sealed using glass fiber reinforced thermosetting epoxy in a glovebox with an oxygen and a water level < 2 ppm (see picture in the Table of Contents).

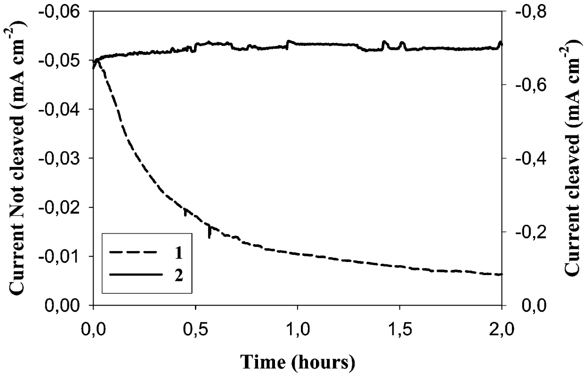

Figure 3. Typical lifetime plots for devices based on polymer **1** and **2** in atmospheric air at 72 °C. The device geometry was ITO−polymer-C_{60}−Al, and the active area was 3 cm^2. Devices based on polymer **1** that has not been cleaved quickly degrade over 1−2 h, whereas devices based on polymer **2** are much more stable.

groups are left on the backbone (i.e., the Chugaev reaction, ene reaction, retro-Diels−Alder, etc.). One possible explanation for our observation of increased lifetime and thermal stability is that the rigidity of the film that is obtained after thermocleavage with the associated increase in film density make diffusion phenomena much slower, whereby stability is increased. A comparison between devices prepared from polymer films that had not been cleaved and those prepared from films that had been cleaved (i.e., films from polymers **1** and **2**) was carried out as shown in Figure 3 with operation of the device in the atmosphere (i.e., no encapsulation or protection of the device). Generally the current densities that could be obtained for devices based on polymer **1** were lower than those based on compound **2** by a factor of about 10. The current density decreased by a factor of 10 in less than 2 h, whereas devices based on polymer **2** generally exhibited an annealing effect where the current density increased over 1−10 h in air (in a vacuum or inert atmosphere this annealing period was generally observed to be 100−1000 h and highly dependent on the temperature).

The high temperatures and light intensities of our testing imply potentially very long lifetimes in a low-light room-temperature application. Using a thermal acceleration factor of 4 between 25 and 72 °C and indoor illumination intensities of 50−100 W m^{-2}, we anticipate operational lifetimes in excess of 20 000 h under the exclusion of water and oxygen.

Acknowledgment. This work was supported by the Danish Technical Research Council (STVF 26-02-0174, STVF 2058-03-0016), the Danish Strategic Research Council (DSF 2104-04-0030), and Public Service Obligation (PSO 103032 FU 3301).

Supporting Information Available: Experimental details of device preparation and device characterization. This material is available free of charge via the Internet at http://pubs.acs.org.

CM051320Q