

An explanation for the high stability of polycarboxythiophenes in photovoltaic devices—A solid-state NMR dipolar recoupling study

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Abstract

Continuous operation of a polymer photovoltaic device under accelerated conditions for more than 1 year has been demonstrated (8760 h at 72 °C, 1000 W m⁻², AM1.5, under vacuum). Formation of hydrogen-bonded networks is proposed to be responsible for the long lifetime and high stability observed in photovoltaic devices employing polythiophene substituted with carboxylic-acid moieties under oxygen free conditions. ¹H and ¹³C solid-state NMR, IR, and ESR spectroscopy of unmodified and isotopically labeled polythiophenes were studied. Distances between the isotopically labeled carboxylic acid carbon atoms were measured by ¹³C solid-state magic-angle-spinning (MAS) NMR using symmetry-based double-quantum (2Q) dipolar recoupling. This revealed the presence of ¹³C–¹³C distances of 3.85 Å, which correspond to the C–C distance in hydrogen-bonded carboxylic acid dimers. In spite of the presence of carboxylic groups in the polymer as demonstrated by ¹³C CP/MAS NMR and IR spectroscopy, the absence of carboxylic protons in solid state ¹H NMR spectra indicate that they are mobile. We link the extraordinary stability of this system to the rigid nature, cross-linking through a hydrogen-bonded network and a partially oxidized state.

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1. Introduction

1.1. The polymer PV technology

Polymer and organic photovoltaics [1–8] show promise as one of tomorrow's renewable energy technologies. The technology offers advantages in terms of production speed, materials cost, weight, thermal budget and is believed to be superior to existing technologies by a considerable margin. The possibilities of solution processing and printing techniques distinguish it from other technologies and give added environmental benefits [9]. So far, the shortcomings of polymer photovoltaics have been their relatively low efficiency and very short lifetime. Recently, polymer photovoltaics have been improved significantly with

efficiencies of around 5% for single junctions [10] and 6.5% for tandem cells [11] while the maximum theoretical efficiency is estimated to be around 30%. The practical limit is anticipated to be in the 10–20% range [12,13]. The demonstration of a very high stability under accelerated conditions has been reported [14,15], and finally large-scale printing of polymer solar cells and solar cell modules has been demonstrated [16–20]. The future success of the polymer PV technology depends on a solution to the central problems of efficiency, stability, and processability. It should also be emphasized that the simultaneous observation of these three factors is still to be demonstrated in the same device or for the same material. The best examples individually show moderate efficiency [10,11], moderate stability [14,15,21], and processing at the 0.1 m² scale [19,20]. The current challenge is thus to combine these three factors in the same material and this is by no means an easy task. Firstly, since efficiency is intimately linked to

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processing, the achievement of a high efficiency hinges on the choice of printing or film-forming method and currently reports make almost exclusive use of spin coating. Secondly, the stability or the properties that convey it are currently very poorly understood so the means for making ends meet is still somewhat undefined.

1.2. Overview of stability issues in polymer photovoltaics

The stability and lifetime of polymer solar cells have in a few reports been detailed. Generally, the device lifetime has been short and the stability poor [22–29]. Of those reports, only a few describe the degradation phenomena that take place in polymer solar cells during operation, and thus, an understanding of the processes that take place is limited [30–39]. The current view is that the polymer photovoltaic as a device is inherently unstable and subject to many possible simultaneous degradation phenomena that may also depend on the history of the device. Thus, it is naïve to propose that a simple methodology will solve the stability problem in organic photovoltaics, and one should view the polymer photovoltaic as a system that is subject to degradation from the moment it is produced. Immediately following the production of the device there are a myriad of chemical, physical, morphological, and mechanical changes that lead to degradation of device performance. Under given circumstances, there are always going to be a few of these mechanisms that are preponderant, and the identification (and possibly elimination) of these will in principle allow for the fabrication of a more stable device. Some of the most important reasons for device instability are oxygen and water from the atmosphere and an elimination of these from the experiment generally leads to more stable devices. Therefore, both water and oxygen are almost always sought excluded in the experiment (but there are exceptions). In a real application, the removal of oxygen and water from the polymer photovoltaic device will almost certainly be required and it is almost impossible to envisage a conjugated organic material that will withstand sunlight, oxygen, and water without undergoing rapid changes. Having eliminated water and oxygen, there is the stability of the device by itself under illumination and in the dark. While the degradation is generally accelerated by temperature and light [40,41], some devices also degrade when left in the dark (especially devices based on polyphenylenevinylene). The general polymer photovoltaic device geometry consists of usually four to five layers (i.e. ITO anode, PEDOT:PSS, active blend, LiF, and Al cathode). This implies several interfaces that can undergo chemical or photochemical reactions leading to poorer charge transport properties with subsequent degradation of device performance. Even if the bulk to the experimenter is virtually unchanged chemically, the device may stop working due to degradation at the interface. The constituents of the individual materials may diffuse through the various layers (i.e. aluminum or ITO from the electrodes may diffuse into the active layers in the device). The

morphology of the device may also change in time leading to degradation of the device performance while no chemical changes have taken place. The experimenter should thus aim at isolating as many of the degradation paths as possible and find explanations for the observed degradation such that solutions can be found which eliminate that particular path (without adversely affecting the overall performance of the device).

1.3. Rigid materials convey long lifetime

An earlier degradation study [30] of polymer photovoltaic devices based on a heterojunction between a PPV and C₆₀ showed through isotopic labeling with ¹⁸O₂, TOF-SIMS analysis and depth profiling that the aluminum electrode gradually dissolves in the active layer and diffuses into it. This was confirmed in later studies on P3HT-PCBM bulk heterojunctions using both ¹⁸O₂ and H₂¹⁸O isotopic labeling [39]. One explanation for the degradation was that the solubilizing sidechains that are added to the conjugated polymer backbone to convey solubility during processing leads to a soft active layer where materials can diffuse. A working hypothesis was thus that if the material could be made harder (i.e. by increasing the glass transition temperature) the device should be more stable. This puts some severe requirements on the active polymer material as it must be possible to process it into the device structure and the current method that is used exclusively is by having solubilizing sidechains substituted onto the conjugated polymer backbone. These sidechains would then have to be removed once incorporated into the device. This removal was made possible by using secondary or tertiary ester groups which eliminate when heated as shown in Fig. 1. Secondary esters eliminate at a somewhat higher temperature than the tertiary ester groups. This implies that upon elimination, a carboxylic acid moiety and an alkene are created and one of them will reside on the conjugated polymer backbone.

Both methods have been explored for the polythiophene backbone leaving either a carboxylic acid on the polythiophene [14,42] or an alkene [15]. While both methods were found to improve the operational stability significantly, the devices with the carboxylic acid moiety attached to the polythiophene backbone were found to give better device performance. Both approaches demonstrate that a rigid system conveyed stability, and a very difficult task has, therefore, been solved. Namely, that the polymer material must be soluble and processable when making the device, followed by a simple chemically non-invasive thermal treatment that converts the soluble material in the device film into an insoluble form. In the process, other changes may take place, i.e. related to morphology, as the density and thickness of the film can change due to weight loss. This is a result of elimination of the sidechain which typically amount to 30–50% of the polymer's weight. The desired solubility transformation is shown schematically in Fig. 2.

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