

Thermo-cleavable solvents for printing conjugated polymers: Application in polymer solar cells

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ABSTRACT

The synthesis and characterization of a number of so-called thermo-cleavable solvents are described with their application in all-air, all-solution and all-screen-printed polymer solar cells. These solvents were developed to meet some requirements for printing techniques such as long “open time” combined with fast drying on heating that cannot be attained with the usual solvents used for conjugated polymers. The new solvents have low volatility at ambient conditions, but decompose thermally at 130–180 °C to low-boiling and highly volatile products. Characterization by thermogravimetric analysis (TGA) and high-temperature NMR established the onset temperature of decomposition, the rate of the reaction and the nature of the products. Printing experiments with inks based on these solvents together with conjugated polymers are exemplified for polymer solar cell devices to show how they enable large-scale production of polymer solar cells using screen printing. Screen-printed solar cells are still very inferior to state of the art P3HT/PCBM technology, but it is our view that it is necessary to explore these printing technologies if polymer solar cells are to ever become commercial products.

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1. Introduction

Research on polymer-based solar cells has attracted interest due to the promise of high-volume production at low cost [1–8]. Most of the efforts have been directed towards improving the power conversion efficiency for small laboratory devices [9–11]. Equally important but less explored areas of research are the stability/degradation [8] and processing issues [12–14]. In principle it should be possible to use simple printing techniques such as screen printing or roll-to-roll slot-die coating to create the layered structure of electrodes and active materials needed. Particularly in screen printing, viscous and non-volatile solvents are used for ink formulations. High viscosity is a prerequisite for successful screen printing, which relies on forcing the ink through a fine mesh. Most conjugated polymer solutions are of low viscosity (i.e. <10 mPa s) making screen printing nearly impossible as the ink simply runs through the open areas of the screen. Low volatility is required since the ink is fully exposed to the atmosphere and smeared over a large surface area during printing, making evaporation of solvents with high volatility fast. For these reasons it is for instance not possible to screen print a solution of P3HT-PCBM in 1,2-dichloro-benzene. Firstly, because the solution has too low viscosity, secondly, because it would simply run

through the screen and thirdly the solvent in the ink would quickly dry, changing the concentration, and possibly dry out in the screen, making repeated printing impossible. It is thus of interest to solve these problems through a custom-made solvent or printing adjuvant with a higher viscosity that allows for an extended handling time in ambient air at around room temperature (RT). After printing, it should be possible to simply remove the solvent (i.e. in an oven), leaving only the print. This may suit many non-critical printing needs. If the substrate or the ink formulation itself cannot withstand very high drying temperatures of solvents with a low volatility, i.e. in combination with oxygen from the atmosphere, problems arise. On the other hand, if the vapor pressure of the solvent could be increased appreciably at a particular temperature threshold by some means the removal of the solvent would become much easier with less impact/degradation of the substrate and ink. We have developed such a solvent system and introduced the concept of thermo-cleavable solvents in a patent [15]. We have then recently employed them in connection with printable polymer solar cells [16]. Several inks based on these principles with active ingredients such as soluble polythiophene or zinc oxide nanoparticles were prepared. A number of printing methods such as screen printing [16], roll-to-roll slot-die coating [17] and pad printing [18] were investigated. The usual solvents for the organic polymer include low-boiling chlorobenzene, 1,2-dichloro-benzene, etc., which are also very noxious substances. Ink formulations based on chlorobenzene or 1,2-dichloro-benzene have been successful for

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creating solar cell devices by techniques where low viscosity and high volatility are not problematic, i.e. spin-coating techniques. Unfortunately such inks are not applicable in the more conventional printing methods such as screen printing, which is generally available as a standard industrial printing technique. The implications of a simple screen-printable polymer solar cell ink would be large as the technology transfer to existing industry would be fast as shown in an example of real polymer solar cell production entirely using screen printing [16]. In addition to the requirement of more viscous inks in the context of screen printing the inks should preferably be non-toxic and less noxious. In case of screen printing there is the special requirement that the ink must not dry out on the mask during the printing. This “open time” may be several hours. On the other hand, once the print has been made it is advantageous to have a short drying time. These seemingly incompatible objectives led us to develop new types of solvents incorporating the thermo-cleavage concept, which could be more suitable for printing polymer solar cells and perhaps other polymer electronics than with conventional techniques. The idea is to incorporate functional groups in the solvent molecules that will cleave them into smaller more volatile fragments. One of the possible reactions that would be suitable is the E1-type elimination of esters, xanthogenates, tertiary amines, S-oxides, etc. as shown in Fig. 1. In the present paper we focus on tertiary esters, which are readily available compounds and where the elimination temperature is in the range of 140–180 °C.

The thermo-cleavage reaction and the products obtained should of course not interfere with other constituents of the ink and thereby degrade the solar cell device properties. Ideally, these products should not have reactive groups and should be volatile and therefore quickly removed at the elimination temperature. Other factors that have to be considered are of course the ability to readily dissolve the organic polymer used, the viscosity at different temperatures, etc.

Conjugated polymers used for organic solar cells have an aromatic (π -conjugated) core that can be excited by light and has high carrier mobility. Solubility is usually imparted by attaching aliphatic side chains, which may even account for most of the

polymer weight. New thermo-cleavable solvents should therefore be able to solubilize each of these types of domains. Another important aspect is the viscosity of the solvent, which should preferably be significantly higher than that for typical solvents such as chloroform and chlorobenzene. Solutions of high molecular weight polymers are usually viscous due to the entanglement of the polymer chains. Many of the experimental polymers that are tested for solar cells are however not of sufficiently high molecular weight to impart enough viscosity and it would therefore be advantageous if the solvent had this property.

Inspiration initially came from a study on polythiophene (P3MHOCT) with side groups that could be removed by a thermo-cleavage reaction (see Fig. 1) [19–25]. This polymer has tertiary ester groups on every second thiophene ring. The ester group is eliminated very rapidly when heated to around 200 °C, leaving the polythiophene with carboxylic acid groups (P3CT). While the thermo-cleavage is fast (minutes) at 200 °C it does take place at lower temperatures of around 140 °C albeit more slowly (hours). The lowest practical temperature of thermo-cleavage is around 140 °C, which fortuitously is compatible with the polymer substrate polyethyleneterephthalate (PET). In the original paper these carboxylic acids were meant to stabilize interaction with an inorganic oxide (TiO₂). Heating the polymer even further to ca 300 °C cleaves of the carboxylic acid groups to give polythiophene itself as shown in Fig. 2 [21,23,24].

The stability increase for devices based on poly(thiophene carboxylic acid) (P3CT) is very remarkable, extending the lifetime of polymer solar cells to beyond 1 year in full sun (AM1.5G) under inert conditions [26,27]. Further studies on the evolution of the solar cell efficiency as a function of the heat treatment show that it is the highest for the ester (P3MHOCT) and the simple polythiophene and the lowest for the carboxylic acid derivative (P3CT) [23]. Stability, on the other hand increases along this series.

2. Experimental

2.1. Materials

3,6-Dimethyl-heptan-3-ol (1a) [28]

The Grignard reagent from 1-bromo-3-methylbutane (96 g, 0.64 mol) was prepared by dropwise addition to magnesium turnings (16.8 g, 0.7 mol) in dry diethyl ether (240 mL) with the addition of five drops of dibromoethane. The mixture was stirred for 1 h to complete the reaction and then 2-butanone (46 g, 0.64 mol) in diethyl ether (240 mL) was added slowly. Stirring was continued overnight and the mixture was then poured into 200 mL dilute hydrochloric acid. The organic layer was separated, washed with water and then dried over magnesium sulfate. Diethyl ether was removed in vacuum to give the

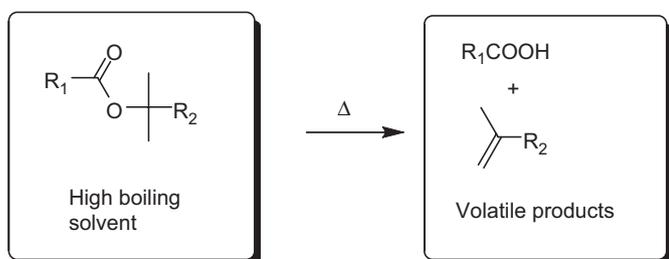


Fig. 1. Illustration of the use of the elimination reaction of tertiary esters in thermo-cleavable solvents. Lower molecular weight products are formed with high vapor pressure/low boiling points.

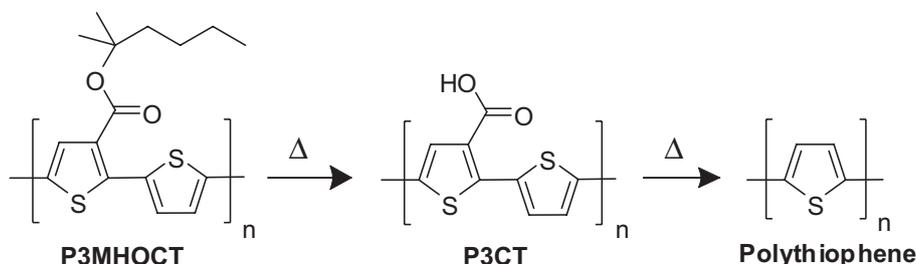


Fig. 2. The polythiophene that led to the introduction of the principle of thermo-cleavability. Soluble P3MHOCT can be sequentially cleaved to P3CT and native polythiophene.

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