Notes

Polythiophene by Solution Processing

Morten Bjerring,[‡] Julie Søgaard Nielsen,[‡]
Niels Chr. Nielsen,[‡] and Frederik C. Krebs*,[†]

The Danish Polymer Centre, RISØ National Laboratory, DK-4000 Roskilde, Denmark, and Center for Insoluble Protein Structures (inSPIN), Interdisciplinary Nanoscience Center (iNANO) and Department of Chemistry, University of Aarhus, DK-8000 Aarhus C, Denmark

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Polythiophene[1] (**1**, PT) is a thermally and chemically stable conjugated polymer material with good electronic properties. Native polythiophene is an insoluble and intractable material, and virtually all reported data for devices based on polythiophenes have been achieved through chemical derivatization of the polythiophene backbone for solubility and processing. One of the most successful polythiophenes is regioregular poly(3-hexylthiophene)[2] (P3HT) which has been employed as the active material in various electronic devices. Some of the highest carrier mobilities observed in conjugated polymers have been reported for P3HT,[3] and many of the efficient[4] and stable[5] polymer-based solar cell devices available today are based on this compound. However, new materials are also starting to appear such as low-band-gap materials[6] and carboxy-substituted polythiophenes for increased operational stability of solar cells in both vacuum and air[7] and for transistors in air.[8] There is an increasing focus on the operational stability of devices while the scientific community traditionally has been content with the reports on the achievement of high performance with little or no mention of stability. Methods for improving the operational stability of devices require an understanding of why degradation takes place.

In transistors the main reason is that the electron-withdrawing carboxylic acid groups lower the position of the highest occupied molecular orbital (HOMO) by about 0.5 eV, thus making doping by oxygen less preponderant. This is seen as the maintenance of a good ON/OFF ratio in air after extended periods of time. The effect of thermally removable solubilizing groups have also been explored in the context of oligothiophenes[9,10] while the effects related to stability and performance in these cases are ascribed to the morphology and organization of the films.

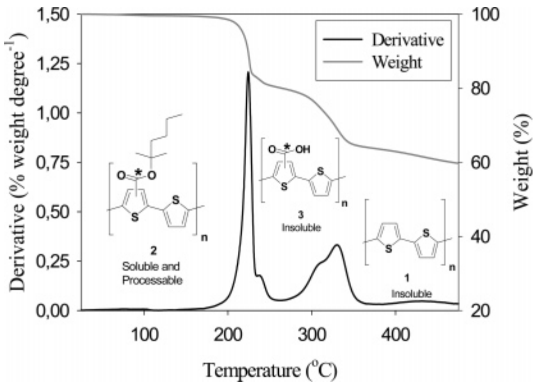

Figure 1. Thermogravimetric data for **2** in the temperature range 25−475 °C. The theoretical weight loss for the two processes are 32% (from **2** to **3**) and 14% (from **3** to **1**), while the observed values are 22% and 13%, respectively. The data were recorded at 50 °C min^{-1}.

Degradation in polymer solar cells is complex, and many mechanisms are in play simultaneously that lead to degradation of device performance. In the absence of oxygen and water, stability can be divided into morphological, physical, chemical, and interface stability. The removal of the solubilizing side chains that are important for processing increases the stability through increasing the glass transition temperature of the polymer in the active layer, making the device more stable in terms of the morphology and the interfaces. Especially diffusion phenomena are important in degradation as shown by TOF-SIMS and isotopic labeling for systems with solubilizing side chains.[11] In the case of polymer solar cells where the solubilizing side chains have been removed, accelerated testing for more than 10 000 h has shown that the interface degradation and diffusion are still important[12] while it has been slowed down to the extent where operation for many years is possible under normal conditions. The link between stability and cross-linking of the system by hydrogen bonding of the carboxylic acid moieties has been proposed[7b] and substantiated.[13]

In terms of device stability, the applications of polymer materials with solubilizing side chains that can be removed are clearly beneficial, and new methodologies to achieve this are needed. The method available today involves tertiary esters that when cleaved thermally leave a carboxylic acid and an alkene. Either of the two may reside on the polymer backbone as shown for oligomers.[10] In this work we report a solid-state study on the thermal behavior of a polythiophene with carboxylic ester groups that can be removed thermally, and we demonstrate how it can be applied to prepare the native polymer material.

Classically, polythiophene has been synthesized electrochemically where thiophene or bithiophene monomers are polymerized oxidatively at the anode or by chemical polymerization. Only the former method has been successful when preparing devices or films for physical studies. So far, there has been no easy route to solution processed unsubstituted polythiophene.

The possibility to "switch off" the solubility of a polythiophene[14] is illustrated in Figure 1 where a soluble polythiophene substituted with tertiary ester groups (**2**) is solution processed into thin films followed by a thermal treatment to eliminate the ester groups, thereby leaving an insoluble carboxy-substituted polythiophene (**3**). During our studies, however, we found two overall weight loss mechanisms in the temperature range from 25 to 475 °C. The first loss peak is in accordance with earlier findings.[14] Employing a steep thermal gradient has the advantage that better distinction between weight loss

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* Corresponding author. E-mail: frederik.krebs@risoe.dk.
[†] RISØ National Laboratory.
[‡] University of Aarhus.

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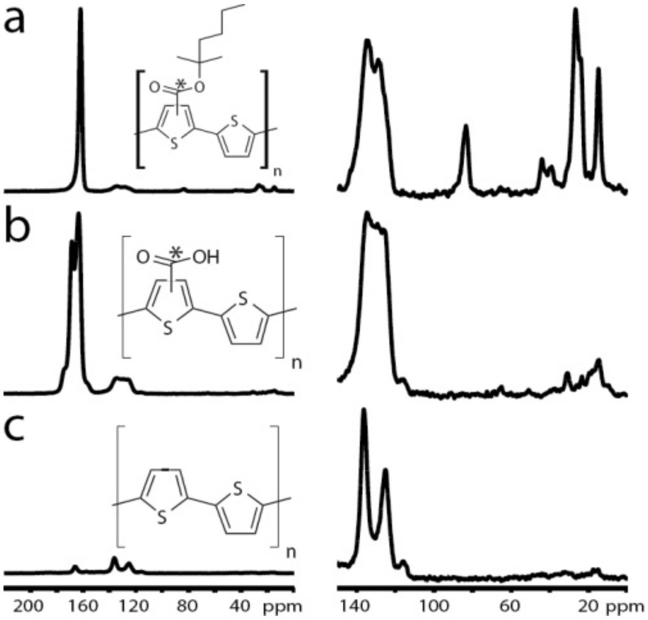

Figure 2. ^{13}C CP/MAS spectra (left) of (a) the ester-functionalized polythiophene, (b) the material heated to 210 °C (carboxypolythiophene), and (c) the material heated above 300 °C (polythiophene) with expansions of the aromatic/aliphatic region to the right.

mechanisms can be made. A disadvantage is that the absolute weight loss has a tendency to be underestimated.

As we anticipate that the thermal behavior is linked mainly to the ester functionality (marked by asterisk in Figure 1), we prepared **2** with ^{13}C-labeling on the carboxylic carbon atom[13,15] for solid-state NMR analysis.[16] Subjecting the labeled material to a temperature of 210 °C under vacuum for 1 h, ^{13}C CP/MAS NMR (Figure 2) shows that most alkyl signals have vanished, leaving ca. 10%. This suggests that some ester groups are not as easily cleaved as the majority. A possible explanation is that the film hardens upon cleavage, and this freezes some of the esters into a less cleavable state. This is supported by the small shoulder toward high temperatures on the first loss peak in Figure 1. The second loss peak from 285 to 350 °C also showed two features which were found to be due to loss of carbon dioxide as supported by IR and NMR of the ^{13}C-labeled material. The ^{13}C CP/MAS NMR spectra in Figure 2 show an almost 100% loss of ^{13}C-labeled material in the second loss peak and simplification of the aromatic peak to contain two distinct signals instead of multiple components in agreement with the proposed structures.

In conclusion, thermal analysis of **2** has shown that the ester groups cleave first followed by the carboxylic acid group. This finding allows us to propose a route to native polythiophene by solution processing which has not been possible hitherto. We believe that this new method may be applied to other polymer and copolymer systems as well and that it will find widespread use. A special feature is that the carboxylic moiety can be removed completely, leaving the native polymer chain without trace of the solubilizing groups.

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Supporting Information Available: Full solid-state NMR spectra as a function of heating and UV−vis spectra as a function of heating. This material is available free of charge via the Internet at http://pubs.acs.org.

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(15) The data for the ^{13}C-labeled polymer used for thermogravimetric measurements and solid-state ^{13}C CP/MAS NMR are $M_w = 8560$, $M_n = 4250$, and PD = 2.013.

(16) We note that an alternative investigation based on ^{1}H MAS NMR of unlabeled material was unsuccessful due to broad ^{1}H resonances.

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