Removal of Palladium Nanoparticles from Polymer Materials[†]

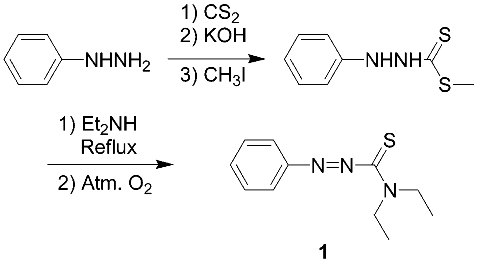
Kim T. Nielsen, Klaus Bechgaard,[‡] and Frederik C. Krebs*

The Danish Polymer Centre, RISØ National Laboratory,
P.O. Box 49, DK-4000 Roskilde, Denmark

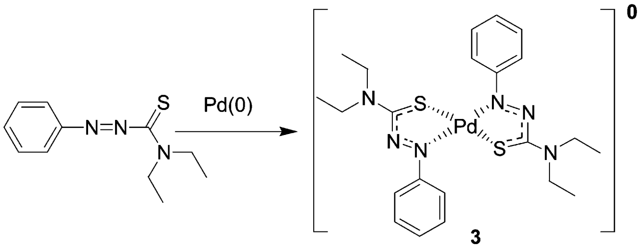
Received November 17, 2004
Revised Manuscript Received December 9, 2004

Palladium catalysis in synthetic organic chemistry has been welcomed as a versatile tool and has made it possible to make complex molecules with many sensitive groups that can be synthesized only under the mild conditions offered by palladium catalysis. The use of palladium in synthetic organic chemistry has led to the development of an arsenal of reaction types that were not possible (or very difficult) without palladium catalysis. The most well-known coupling reactions are Heck,[1] Stille,[2] Suzuki,[3] Negishi,[4] and Sonogashira,[5] and while many more exist they are variations over the general theme. An often neglected fact is the formation of palladium nanoparticles during the chemical reactions when the catalyst degrades. When the product of the chemical reaction can be purified by distillation (or for small molecules crystallized), it is often possible to obtain a palladium-free product. For large molecules and polymers, however, these means of purification are not available, and a contamination of the product with palladium should always be assumed. The extent to which palladium nanoparticles are withheld in the product depends on how strong the affinity for palladium is. As an example, palladium nanoparticles bind well to conjugated polymers, leading to a product with palladium that cannot be completely removed using current purification techniques. While the contaminant palladium nanoparticles/catalyst to a large extent can be removed, the crude product typically contains palladium nanoparticles/catalyst. The palladium contamination (0.0001−1% w/w) often goes by unnoticed or undetected, as it does not interfere with common analytical techniques (elemental analysis, NMR, etc.). When, however, the electrical properties of the product are important, even the smallest contamination has a detrimental effect on thin film device performance. We recently discovered[6] the problem for a poly(phenylenevinylene) product prepared by two different routes: an elaborate palladium-free route and a one-step palladium route based on the Heck reaction. The polymer products were identical in most physical−chemical aspects (NMR, UV−vis absorption, etc.), but when electroluminescent devices were made using the polymer product from the palladium route, they were not functional whereas the non-palladium product gave functional devices. The lack of functionality was observed as a very low device resistance and the absence of electroluminescence. We later demonstrated the same problem for poly(phenyleneethynylene)s prepared by a palladium route following Sonogashira conditions.[7] We attempted to remove the palladium contamination using N,N-diethyldithiocarbamate (**2**) and found that we were able to remove the palladium to a level where device fabrication was possible.[7,8] The shortcoming of **2**, however, was that prolonged reaction times altered the photophysical properties of the poly(phenyleneethynylene) product to an extent where the desired electroluminescence became suppressed. The device resistance, however, remained high.

Scheme 1



Scheme 2



The efficient chemical removal of palladium nanoparticles/catalyst is not a trivial task if the desired organic product is to be left unaffected, and while **2** provided a partial solution and has been employed successfully for removal of palladium during solid-phase synthesis,[9] a new procedure was highly desirable. Various approaches to the removal of heavy metals using *N*-acylcysteine, polystyrene-based thiuronium salts, or silica particles bearing pendant alkyl groups with terminal thiol functionalities have been reported.[10] While they bind palladium efficiently, they do not work well for polymer products since a large proportion of the polymer product is absorbed by the silica or polymer media. A solubilizing agent would thus be more appropriate. Azothioformamides have been reported to dissolve metals like zinc and cadmium in the form of their amalgam and Ni(0) compounds through $Ni(CO)_4$ and $Ni(P(OEt)_3)_4$.[11,12] We decided to attempt the use of azothioformamides to dissolve palladium nanoparticles/catalyst.

While the synthesis of **1** has been reported,[11] we devised a simple one-pot synthesis giving the same yield of **1** as shown in Scheme 1. Compound **1** was shown to efficiently dissolve palladium nanoparticles directly. This could be monitored as a change in color from the light orange color of **1** to a dark brown-green color of **3**. It should be emphasized that **1** also dissolves other metals directly (Cu, Ni, Pt), but we focus on the palladium context here. The neutral complex that is formed in the heterogeneous reaction of Pd nanoparticles and **1** is shown in Scheme 2.

Compound **3** is stable in air and readily soluble in most organic solvents such as methanol, chloroform, light petroleum, etc. The synthetic approach of Scheme 1 is general, and many different substituents to the

---

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

[‡] Department of Chemistry, University of Copenhagen, DK 2100, Denmark.

* Corresponding author: e-mail frederik.krebs@risoe.dk.

10.1021/ma047635t CCC: $30.25

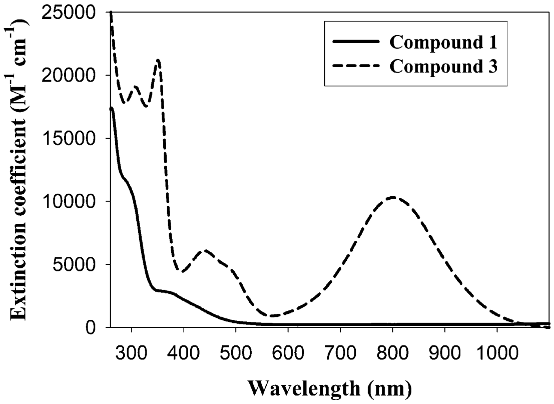


Figure 1. UV−vis spectrum of **1** and **3** in chloroform at room temperature showing their extinction coefficients. Compound **3** shows a moderately strong absorption with a maximum at 801 nm where compound **1** does not absorb, making this technique applicable for the analytical determination of residual palladium content in materials where palladium catalysis has been employed.

azothioformamide skeleton can be envisaged that can encompass different solubility requirements of the derived palladium complexes, making its removal easy in terms of solubility/insolubility. Having demonstrated the successful reaction of **1** with metallic palladium nanoparticles/catalyst it remained to evaluate possible side reactions of **1** with the conjugated polymer product. The most likely reaction between an unsaturation such as vinylene or ethynylene groups is an electrocyclic condensation reaction of the Diels−Alder type. We performed model reactions between **1** and stilbene or tolane in both the presence and absence of palladium. We were not able to demonstrate detectable amounts of the corresponding electrocyclic condensation products (see Supporting Information). The major problem with such side reactions during polymer synthesis is that they are accumulated, and their alleviation is difficult to envisage. The removal of palladium using **1** is thus possible. While the treatment can be performed at elevated temperature, it works best at room temperature and was normally complete within 1 h. The progress of the palladium dissolution could be conveniently followed using simple UV−vis spectroscopy. This has the advantage that the complex exhibits a moderately strong absorption in a wavelength region normally not explored for saturated polymers and rarely for conjugated polymers and organic materials ($\epsilon_{797\mathrm{nm,THF}} = 8500\ \mathrm{M}^{-1}\ \mathrm{cm}^{-1}$, $\epsilon_{801\mathrm{nm,chloroform}} = 10\,300\ \mathrm{M}^{-1}\ \mathrm{cm}^{-1}$). The method presented here can thus be used for preparative work where alleviation of residual palladium catalyst is of interest and for analytical purposes where the palladium content can be determined by simple treatment with **1** followed by UV−vis analysis. In the case where there is an overlap, a correct analytical determination of the palladium content is still possible provided that the UV−vis spectrum of the sample is known and can be accurately subtracted.

We have shown the applicability of **1** for the removal of residual palladium catalyst through **3** that in our case is a complex readily soluble in common organic solvents including methanol commonly used to precipitate polymer materials. Using the method of analysis presented here, it is possible to determine the palladium content with a detection limit of 0.1 ppm (w/w) using 50 mg sample. Employing larger samples and concentration of the supernatant the detection limit can be lowered to 1 ppb (w/w). The results are summarized in Table 1.

Table 1. Palladium Content before and after Treatment with 1 for Polymer Samples of the Poly(phenylenevinylene), Poly(phenyleneethynylene), and Poly(alkylthiophene) Type and the Device Resistance According to the Device Geometry (See Supporting Information)

polymer	Pd content before/after (ppm)	resistance before/after (kΩ)
PPV	17860/<0.1	0.10/30
PPE	268/<0.1	0.03/45
PAT	4073/<0.1	0.06/24

The polymers employed for the demonstration were prepared by typical palladium routes (see Supporting Information) and cover a broad range of conjugated polymers: poly(phenylenevinylene) (PPV), poly(phenyleneethynylene)s (PPE), and poly(alkylthiophene) (PAT). While the palladium content depends on the amount of catalyst used and on the conditions of the experiment, the levels observed before treatment are typical. Removal using **1** is efficient, and this is reflected in the device resistance and device function. Electroluminescent and photovoltaic devices could be prepared after palladium removal using this method.

In conclusion, our report describes the efficient removal of the palladium nanoparticle/catalyst contained in polymer materials by a palladium route. We further demonstrate the possibility of a quantitative determination of the palladium nanoparticles/catalyst content at the 1 ppb (w/w) level using simple UV−vis spectrophotometry. It should be emphasized that the method is general and that it can be applied to any sample, small molecule or macromolecular. The only requirement is solubility of the sample.

Acknowledgment. The work was supported by the Danish Technical Research Council (STVF).

Supporting Information Available: Details of the one-pot synthesis to **1**, preparation of **3**, general procedure for the removal of palladium remnants from conjugated polymer materials, analysis of the palladium content in a conjugated polymer sample at the 0.1 ppm level, the device geometry, and UV−vis in THF. This material is available free of charge via the Internet at http://pubs.acs.org.

References and Notes

(1) Dieck, H. A.; Heck, F. R. *J. Organomet. Chem.* **1975**, *93*, 259−263.
(2) Milstein, D.; Stille, J. K. *J. Am. Chem. Soc.* **1978**, *100*, 3636−3638.
(3) Suzuki, A. *Acc. Chem. Res.* **1982**, *15*, 178−184.
(4) Negishi, E.; King, A. O.; Okukado, N. *J. Org. Chem.* **1977**, *42*, 1821−1823.
(5) Sonogashira, K.; Tohda, Y.; Hagihara, N. *Tetrahedron Lett.* **1975**, *50*, 4467−4470.
(6) Krebs, F. C.; Nyberg, R. B.; Jørgensen, M. *Chem. Mater.* **2004**, *16*, 1313−1318.
(7) Nielsen, K. T.; Spanggaard, H.; Krebs, F. C. *Macromolecules*, in press.
(8) Nielsen, K. T.; Spanggaard, H.; Krebs, F. C. *Displays*, in press.
(9) Jones, L.; Schumm, J. S.; Tour, J. M. *J. Org. Chem.* **1997**, *62*, 1388−1410.
(10) Schmuckler, G. German Patent 15 33 131, 1974. Villa, M.; Cannata, V.; Rosi, A.; Allegrini, P. International Patent WO 98/51646. Königsberger, K.; Chen, G.-P.; Wu, R. R.; Girgis, M. J.; Prasad, K.; Repič, O.; Blacklock, T. J. *Org. Proc. Res. Dev.* **2003**, *7*, 733−742.
(11) Jensen, K. A.; Bechgaard, K.; Pedersen, C. T. *Acta Chem. Scand.* **1972**, *26*, 2913−2922.
(12) Bechgaard, K. Thesis, Copenhagen, 1973.

MA047635T