Chem. Mater. **2004,** *16,* 1313−1318

Influence of Residual Catalyst on the Properties of Conjugated Polyphenylenevinylene Materials: Palladium Nanoparticles and Poor Electrical Performance

Frederik C. Krebs,* René B. Nyberg, and Mikkel Jørgensen

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

Received November 21, 2003. Revised Manuscript Received January 20, 2004

The synthesis of conjugated polymer materials using palladium catalysis was shown to result in a contamination of the polymer product with palladium nanoparticles that were difficult to detect and remove. The particle size was on the order of 20 nm, as evidenced by transmission electron microscopy (TEM). Further, electron spectroscopy for chemical analysis (ESCA), powder X-ray diffraction, and scanning electron microscopy (SEM) were employed to establish the chemical and physical nature of the catalyst remnants. We demonstrate the identity of many physical and chemical properties of the same polymer material prepared by two different routes: the palladium route and the condensation route. The performance in a device application of the two polymer materials was, however, very different, and the palladium route was demonstrated to give poor films with low breakdown voltages and short circuits.

Introduction

The field of electroactive polymers has grown during the past 15 years. The flexibility housed in the synthetic organic chemical approach has resulted in their application as the functional material in many different devices, such as polymer-based photovoltaics,[1] polymer-based light emitting diodes,[2] and all-polymer electronic circuits.[3] From the synthetic point of view, this has led to many different approaches to the efficient synthesis of conjugated polymer materials using widely different monomer molecules. Traditionally, condensation polymerizations were employed and the most successful of these are probably the Gilch method,[4] the Wessling method,[5] and the Durham method.[6] In recent years, transition-metal catalysis has become very popular and this has allowed for the synthesis of more complex polymer systems. The most widely used metal catalyst is palladium in the form of complexes with organic ligands that via Suzuki,[7] Heck,[8] Sonogashira,[9] Stille,[10] and Negishi[11] reaction types on bifunctional monomers give conjugated polymers. There are a few other examples of conjugated polymer synthesis using different transition metals, most notably nickel[12] and rhodium

---

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

(1) Yu, G.; Gao, J.; Hummelen, J. C.; Wudl, F.; Heeger, A. J. *Science* **1995**, *270*, 1789−1791. Halls, J. J. M.; Walsh, C. A.; Greenham, N. C.; Marseglia, E. A.; Friend, R. H.; Moratti, S. C.; Holmes, A. B. *Nature* **1995**, *376*, 498−500. Granström, M.; Petritsch, K.; Arias, A. C.; Lux, A.; Andersson, M. R.; Friend, R. H. *Nature* **1998**, *395*, 257−260. Roman, L. S.; Mammo, W.; Pettersson, L. A. A.; Andersson, M. A.; Inganäs, O. *Adv. Mater.* **1998**, *10*, 774−777. Dittmer, J. J.; Marseglia, E. A.; Friend, R. H. *Adv. Mater.* **2000**, *12*, 1270−1274. Zhang, F.; Johansson, M.; Andersson, M. A.; Hummelen, J. C.; Inganäs, O. *Adv. Mater.* **2002**, *14*, 662−665. Huynh, W. U.; Dittmer, J. J.; Alivisatos, A. P. *Science* **2002**, *295*, 2425−2427. Dittmer, J. J.; Lazzaroni, R.; Leclérc, Ph.; Moretti, P.; Granström, M.; Petritsch, K.; Marseglia, E. A.; Friend, R. H.; Brédas, J. L.; Rost, H.; Holmes, A. B. *Sol. Energy Mater. Sol. Cells* **2000**, *61*, 53−61. Petritsch, K.; Dittmer, J. J.; Marseglia, E. A.; Friend, R. H.; Lux, A.; Rozenberg, G. G.; Moratti, S. C.; Holmes, A. B. *Sol. Energy Mater. Sol. Cells* **2000**, *61*, 63−72. Sariciftci, N. S.; Braun, D.; Zhang, C.; Srdanov, V. I. V. I.; Heeger, A. J.; Stucky, G.; Wudl, F. *Appl. Phys. Lett.* **1993**, *62*, 585−587. Shaheen, S. E.; Brabec, C. J.; Sariciftci, N. S.; Padinger, F.; Fromherz, T.; Hummelen, J. C. *Appl. Phys. Lett.* **2001**, *78*, 841−843. Yu, G.; Zhang, C.; Heeger, A. J. *Appl. Phys. Lett.* **1994**, *64*, 1540−1542.

(2) Ho, P. K. H.; Kim, J.-S.; Burroughes, J. H.; Becker, H.; Li, S. F. Y.; Brown, T. M.; Cacialli, F.; Friend, R. H. *Nature* **2000**, *404*, 481−484.Yang, Y. *Mater. Res. Soc. Bull.* **1997**, *22*, 16−24. Huitema, H. E. A.; Gelinck, G. H.; van der Putten, J. B. P. H.; Kuijk, K. E.; Hart, C. M.; Cantatore, E.; Herwig, P. T.; van Breemen, A. J. J. M.; de Leeuw, D. M. *Nature* **2001**, *414*, 599.

(3) Katz, H. E.; Lovinger, A. J.; Johnson, J.; Kloc, C.; Siegrist, T.; Li, W.; Lin, Y.-Y.; Dodabalapur, A. *Nature* **2000**, *404*, 478−480. Drury, C. J.; Mutsaers, C. M. J.; Hart, C. M.; Matters, M.; de Leeuw, D. M. *Appl. Phys. Lett.* **1998**, *73*, 108−110. Sirringhaus, H.; Tessler, N.; Friend, R. H. *Science* **1998**, *393*, 619−620.

(4) Gilch, H. G.; Wheelwright, W. L. *J. Polym. Sci., Part A* **1966**, *4*, 1337.

(5) Wessling, R. A. *J. Polym. Chem., Polym. Symp.* **1985**, *72*, 55.

(6) Feast, W. J.; Winter, J. N. *J. Chem. Soc. Chem. Commun.* **1985**, 202−203.

(7) Donat-Bouillud, A.; Lévesque, I.; Tao, Y.; D'Iorio, M.; Beaupré, S.; Blondin, P.; Ranger, M.; Bouchard, J.; Leclerc, M. *Chem. Mater.* **2000**, *12*, 1931−1936.

(8) Wang, S.; Oldham, W. J., Jr.; Hudack, R. A., Jr.; Bazan, G. C. *J. Am. Chem. Soc.* **2000**, *122*, 5695−5709. Zotti, G.; Schiavon, G.; Zecchin, S.; Morin, J.-F.; Leclerc, M. *Macromolecules* **2002**, *35*, 2122−2135.

(9) Moore, J. S.; Zhang, J. S. *Angew. Chem.* **1993**, *31*, 922−924. Ofer, D.; Swager, T. M.; Wrighton, M. S. *Chem. Mater.* **1995**, *7*, 8−425. Zhou, Q.; Swager, T. M. *J. Am. Chem. Soc.* **1995**, *117*, 12593−12602. Ramos, A. M.; Rispens, M. T.; van Duren, J. K. J.; Hummelen, J. C.; Janssen, R. A. J. *J. Am. Chem. Soc.* **2001**, *123*, 6714−6715.

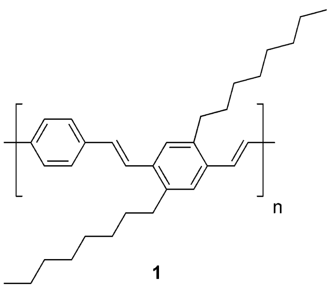
(10) Lère-Porte, J.-P., Moreau, J. J. E., Torreilles, C. *Eur. J. Org. Chem.* **2001**, 1249−1258. Dhanabalan, A.; van Dongen, J. L. J.; van Duren, J. K. J.; Janssen, H. M.; van Hal, P. A.; Janssen, R. A. J. *Macromolecules* **2001**, *34*, 2495−2501.

(11) Wang, F.; Wilson, M. S.; Rauh, R. D.; Schottland, P.; Reynolds, J. R. *Macromolecules* **1999**, *32*, 4272−4278.

(12) Yamamoto, T.; Hayashi, Y.; Yamamoto, A. *Bull. Chem. Soc. Jpn.* **1978**, *51*, 2091−2097. Nurulla, I.; Morikita, H.; Fukumoto, H.; Yamamoto, T. *Macromol. Chem. Phys.* **2001**, *202*, 2335−2340.

10.1021/cm035205w CCC: $27.50

Scheme 1



1

catalysts,[13] that offer the possibility of a polymerization that is “living” such that conjugated block copolymers[14] can be synthesized. Finally there are examples of methathesis reactions giving conjugated polymer systems.[15]

Recently, we reported the synthesis and properties of a new type of polyphenylenevinylene (PPV) with every second phenylene ring having dialkyl substituents. This material was prepared by a condensation polymerization reaction that gave a very pure polymer product. The purity and regularity was reflected in very desirable properties, the most important being a high degree of crystallinity, exceedingly high charge carrier mobility, and very long charge carrier lifetimes.[16]

In this paper we present chemical and physical similarities and differences of the polymer material shown in Scheme 1 when prepared by two different methods, condensation polymerization and palladium-catalyzed polymerization. We further demonstrate that the palladium-catalyzed polymerization give rise to a product contaminated with palladium nanoparticles that are not easily removed and that has a severe influence on many of the physical properties pertaining to efficient device construction and efficiency.

Though palladium-catalyzed syntheses of conjugated polymers are ubiquitous, no specific comments on the deleterious effects of residual palladium particles have been found to our knowledge. Some evidence for palladium metal nanoparticle impurities can however be seen in reported X-ray diffractograms.[17]

Experimental Section

Synthesis. Polymer **1a** was prepared as described in ref 16, polymer **1c** was prepared as described in ref 20. Size exclusion chromatography (SEC) was performed in THF solution and the molecular weights calculated using a calibration curve based on polystyrene standards.

Poly-1,2‴-(2,5-dioctyl-1,4-phenylene-1′,2′-vinylene-1″,4″-phenylene-1‴,2‴ -vinylene) (1b). Pd$_2$(dba)$_3$ (50 mg, catalyst) and tri-*tert*-butylphosphine tetrafluoroborate (50 mg, ligand) were placed in a 100 mL flask. THF (50 mL) that had been passed through alumina was added and the mixture was purged with argon for 5 min. *N*-Methyldicyclohexylamine (1 mL, excess) was added and argon purging continued. 1,4-Dibromo-2,5-dioctylbenzene (2.3 g, 5 mmol) and 1,4-divinylbenzene (0.65 g, 5 mmol) were added, and the mixture was heated to reflux. After 24 h, the mixture was filtered through a 2.7 μm filter into methanol to precipitate the bright yellow product. It was then filtered and dried to give a yellow solid in 89% yield (1.98 g). ^{1}H NMR (250.1 MHz, C$_6$D$_4$Cl$_2$, 400 K, TMS) δ: 0.90 (broad singlet, 6H), 1.3−1.6 (m, 20H), 1.8 (broad singlet, 4H), 2.8 (broad singlet, 4H), 6.9−7.6 (m, 10H). M_p = 3440. M_n = 4070. M_w/M_n = 2.22.

Photophysical Methods. The UV−vis spectra were recorded on films spin coated onto microscope glass slides from a 6 mg mL^{-1} solution in chlorobenzene.

Device Preparation. ITO−polymer−aluminum devices were prepared as described in ref 21. This involved formation of the conducting ITO pattern (surface resistance < 30 Ω) by etching using a mixture of HCl (aq, 20%) and HNO$_3$ (aq, 5%) at 55 °C for typically 60 s. The ITO slides were then cleaned in 2-propanol by ultrasonication for 20 min and blown dry in a stream of argon prior to spin-coating of either polymer or PEDOT:PSS solution (Aldrich, 1.3 wt % aqueous solution) containing sorbitol (2.5 mg mL^{-1}). In the case of PEDOT:PSS-covered substrates, after spin-coating (at 1500 rpm) they were heated in an oven at 120 °C for 2 h and used directly. ITO−PEDOT:PSS−polymer−aluminum devices were prepared as described in ref 20. Spin-coating was performed in air and the freshly prepared polymer films were transferred to the metal evaporator directly after preparation and subjected to characterization without annealing. Annealing in a vacuum oven at 80 °C was attempted but had no significant effect on the device resistance.

Isolation and Analysis of the Palladium Nanoparticles. The palladium nanoparticles were obtained by dissolving the polymer in boiling chlorobenzene (10 mg mL^{-1}) and five subsequent cycles of centrifugation, decanting of the supernatant, resuspension, and boiling in chlorobenzene. The particles were kept in chlorobenzene. Analysis of the particles using ESCA showed exclusively the presence of only palladium using a Sage 100 instrument from Specs. SEM was performed on a JEOL-840 equipped with an EDX Voyager from Noran. The EDX showed almost exclusively the presence of palladium and trace amounts of carbon. TEM was performed by resuspending the particles in ethanol and transferring them onto a copper grid using a JEOL-2000FX. Powder X-ray diffraction on the palladium particles was performed by placing the sample in a 1.0 mm capillary and rotating the capillary during exposure with Cu Kα radiation on a RAPID diffractometer from RIGAKU/MSC. The image plate data was background subtracted and integrated using the AreaMax program from RIGAKU/MSC.

Results and Discussion

Synthesis. The synthesis of the polymer **1** (Scheme 1) reported in ref 16 was carried out by a condensation polymerization reaction employing a highly purified dialdehyde and a diphosphonate ester. Since the preparation of the pure dialkyldiformylbenzene monomer for that reaction was quite tedious, the desire to find a more straightforward route employing palladium catalysis in a Heck type reaction was obvious. We have prepared **1** using two different palladium catalyzed polymerization reactions, as shown in Scheme 2. The simplest one employs a readily available dibromodialkylbenzene and

---

(13) Misumi, Y.; Masuda, T. *Macromolecules* **1998**, *31*, 7572−7573. Misumi, Y.; Kanki, K.; Miyake, M.; Masuda, T. *Macromol. Chem. Phys.* **2000**, *201*, 2239−2244. Kishimoto, Y.; Eckerle, P.; Miyatake, T.; Kainosho, M.; Ono, A.; Ikariya, T.; Noyori, R. *J. Am. Chem. Soc.* **1999**, *121*, 12035−12044.

(14) Krebs, F. C.; Jørgensen, M. *Polym. Bull.* **2003**, *50*, 359−366.

(15) Brizius, G.; Pschirer, N. G.; Steffen, W.; Stitzer, K.; zur Loye, H.-C.; Bunz, U. W. F. *J. Am. Chem. Soc.* **2000**, *122*, 12435−12440.

(16) Krebs, F. C.; Jørgensen, M. *Macromolecules* **2003**, *36*, 4374−4384.

(17) Bao, Z.; Chen, Y.; Cai, R.; Yu, L. *Macromolecules* **1993**, *26*, 5281−5286.

(18) Krebs, F. C.; Jørgensen, M. *Macromolecules* **2002**, *35*, 7200−7206.

(19) Krebs, F. C.; Jørgensen, M. *Macromolecules* **2002**, *35*, 10233−10237.

(20) Krebs, F. C.; Hagemann, O.; Jørgensen, M. *Sol. Energy Mater. Sol. Cells* **2004**, in press.

(21) Krebs, F. C.; Jørgensen, M. *Rev. Sci. Instr.* **2003**, *74*, 3438−3441.

Scheme 2

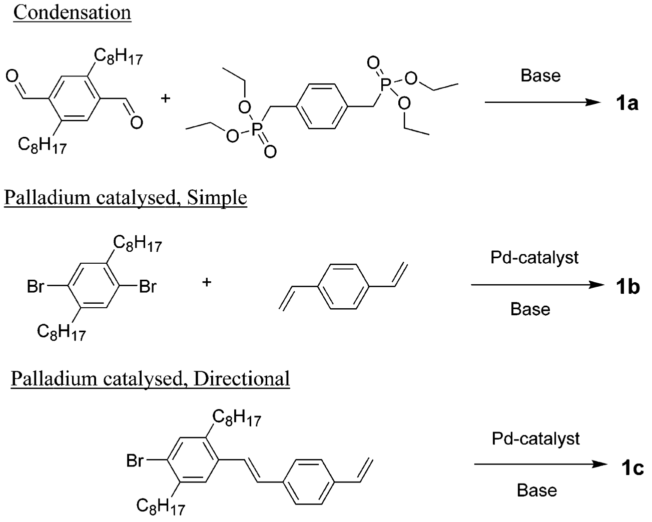


Table 1. Comparison of the Film and Polymer Properties[a]

compd	V_{oc} (mV)[b]	I_{sc} (mA cm^{-2})[b]	resistance (kΩ)[c]	λ_{max}, film (nm)	M_n	M_p	M_w/M_n
1a	85	−0.5	110	437[d]	26400[d]	14000[d]	3.18[d]
	(110)	(−0.5)	(125)				
1b	0.02	−0.25	0.03	414	4070	3440	2.22
	(0.09)	(−1.2)	(0.08)				
1c	0.02	−0.25	0.03	415	6870[e]	13800[e]	2.88[e]
	(0.13)	(−0.9)	(0.132)				
1c[f]	(0.16)	(−0.9)	(0.157)				

[a] The results are from photovoltaic experiments, film resistances in the photovoltaic device geometry, absorption maxima for the films, and the molecular weight distributions from solvent exclusion chromatography (SEC) based on a polystyrene standard series. Values in brackets were obtained from devices where the ITO electrode was covered by a layer of 100 nm layer of PEDOT:PSS before spin coating the conjugated polymer material. [b] Illumination at 440 nm. [c] Measured in the dark. [d] Taken from ref 16. [e] Taken from ref 20. [f] Ultracentrifuged.

divinylbenzene and gave polymer **1b**. The strategy is similar to the one reported in the literature.[17] The second one is one component and more elaborate but does provide the possibility for directional synthesis,[18−20] thus allowing for growth of a conjugated polymer chain from a suitable initiator. This polymerization reaction using the monomer on its own gave polymer **1c** and has for instance been applied for the synthesis of a dye-linked conjugated block copolymer and a dye-linked conducting homopolymer.[20] These molecular architectures can only be arrived at by use of a directional polymerization scheme.

Conventional Characterization. The polymers **1a**, **1b**, and **1c** were obtained in a form where most of the properties normally investigated by synthetic chemists were identical. The NMR spectra were very similar, except for the signals from the different end groups (see Supporting Information). Also, the photophysical properties, molecular weights, and polydispersity were comparable (see Table 1). The general trend was however a red-shifted absorption maximum, higher molecular weight, and larger polydispersity for the condensation polymer **1a**. A particular concern was the possibility of 1,1-addition to the vinyl groups during the Heck reactions, but we were unable to detect this and presume that if this does take place it is to a negligible extent.

Electrical Properties of Thin Films. The most notable difference was observed when attempting to make simple one-layer photovoltaic devices based on the polymer materials with aluminum as the low work function electrode and indium−tin oxide (ITO) as the transparent electrode. We used the same procedure and device geometry presented elsewhere.[21] Devices based on **1a** gave a large internal resistance of typically 110 kΩ with an optical density of 0.25 and a photovoltaic response typical of a homopolymer device with an open circuit voltage (V_{oc}) of 85 mV and a short circuit current (I_{sc}) of 0.5 μA cm^{-2}.

Devices based on **1b** or **1c**, however, gave a very low resistance (when having an optical density of 0.25) of around 30 Ω that essentially corresponds to a short circuit (or multiple short circuits in series with the device resistance of around 30 Ω). Some of the properties of the polymers are summarized in Table 1. We also prepared devices using PEDOT:PSS-coated ITO substrates to eliminate (or reduce) the effect of possible pinholes in the polymer films that would lead to direct ITO−aluminum contacts. While the PEDOT:PSS barrier layer increased the device resistance 5-fold (from a typical 30 Ω resistance in the case of an ITO−aluminum dummy device to a typical 150 Ω resistance in the case of a ITO−PEDOT:PSS−aluminum dummy device), the device resistances in the presence of the appropriate conjugated polymer material was increased accordingly. We also attempted to simply test the devices with the PEDOT:PSS barrier layer for electroluminescence. In the case of **1a**, the devices emitted light homogeneously over the large area (3 cm^2) of mutual electrode overlap at low turn on voltages, indicating that the voltage drop is over the polymer film and not limited by the device series resistance. In the case of electroluminescent devices based on **1b** and **1c**, it was possible to observe electroluminescence, but very large voltages and currents were required. Further, the electroluminescence was weak and light was not emitted homogeneously. Only a small line, defined by the area where the two electrodes meet, emitted light, indicating that the voltage drop is in the device electrodes and current is passed in a very small area of the film. These observations are to be expected in the case of efficient short circuits in the devices making the serial resistance of the device electrodes larger than the film resistance. The largest voltage drop is thus in the electrodes.

Analysis and Evidence of Metallic Palladium Nanoparticles. We performed electron spectroscopy for chemical analysis (ESCA) on thin polymer films based on **1a**, **1b** and **1c** and at first got a negative result, showing no indication of any palladium content. The reason for this could be that the palladium material does not extend toward the surface. Microfiltration of the polymer solutions removed a black residue that was identified as palladium using ESCA. To obtain a reasonable amount of this black residue for further analysis, we decided to subject the polymer solution to ultracentrifugation to isolate the black material. Analysis again revealed a large palladium content. Scanning electron micrographs combined with energy-dispersive X-ray spectroscopy (EDX) of the black residue showed

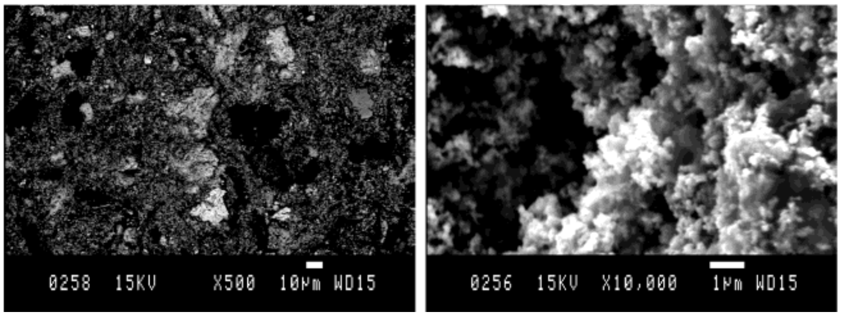


Figure 1. A scanning electron micrograph image of the black residue as isolated from a polymer solution using ultracentrifugation. The image on the left was recorded in backscattering mode, and the image on the right is a secondary electron image at higher resolution.

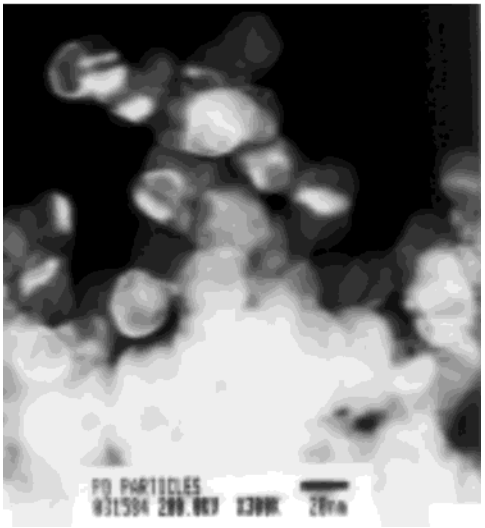


Figure 2. A transmission electron micrograph of the black residue as isolated from a polymer solution using ultracentrifugation. Toward the edges of the aggregates the particles are clearly seen to have diameters close to 20 nm, as indicated by the bar on the image.

it to be consisting of virtually pure palladium and gave images as shown in Figure 1.

The SEM images did not allow for the observation of discrete particles but did seem to indicate the presence of very small particles that might be able to pass through a microfilter with a pore diameter of 1 μm. We subsequently obtained a transmission electron micrograph (TEM) to possibly determine the size of the particles. The black residue was transferred to a copper grid by suspension in ethanol, deposition, and finally drying. A good image could be obtained at the edges of the aggregates, as shown in Figure 2, where the particle size is clearly seen to be on the order of 20 nm, thus excluding the possibility of microfiltration as a means of purifying the material. While ESCA gave proof of the chemical content of the black residue as being mainly palladium, we recorded an X-ray powder diffractogram of the black residue to confirm that the chemical state of palladium was metallic. The X-ray powder diffractogram, as shown in Figure 3, confirmed the presence of metallic palladium nanoparticles, as evident from the line width of the peaks.[22]

On the basis of the evidence given above, it is clear that polymer synthesis using palladium catalysis will always lead to palladium nanoparticles or nanocrystals that are difficult to remove by simple filtration. The particles that we isolated by ultracentrifugation were soluble in organic solvents, which could indicate that some conjugated polymer material is adsorbed to the surface of the palladium nanoparticles, thus acting as solubilizing side chains. This behavior is quite commonly observed for nanoparticles. The solubility of gold nanoparticles with organic molecules adsorbed to the surface in common solvents is quite high, allowing for spectroscopical analysis and even size exclusion chromatography.[23]

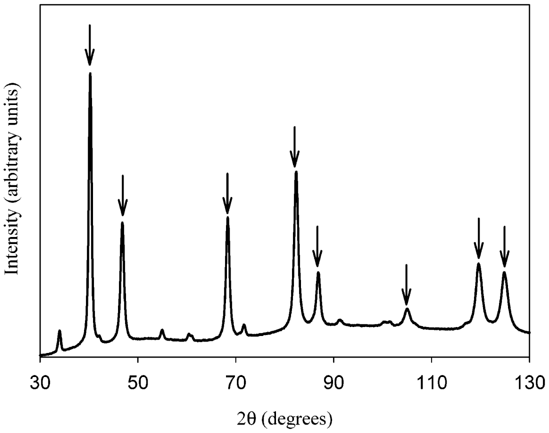


Figure 3. An X-ray powder diffractogram of the black residue showing the characteristic peaks of palladium metal (marked with an arrow) and a line width typical of nanoparticles. There are some minor impurity peaks.

Effect of Palladium Nanoparticles on the Performance of Electroactive Devices. The poor electrical performance of electroactive devices based on **1b** and **1c** as compared to devices based on **1a** was ascribed to efficient short circuits. The presence of palladium nanoparticles or small aggregates could be the cause of the short circuits. To support this idea the resistance through a palladium nanoparticle with a diameter of 20 nm spanning two electrodes is on the order of 4 Ω and thus considerably smaller than the device resistance, which was found to be on the order of 30 Ω for ITO−aluminum devices and 150 Ω for ITO−PEDOT:PSS−aluminum devices. The device resistance is thus expected to be dominated by the ITO−aluminum or the ITO−PEDOT:PSS−aluminum resistance with the pal-

---

[22] Kaszkur, Z. *J. Appl. Crystallogr.* **2000**, *33*, 1262−1270.

[23] Novak, J. P.; Nickerson, C.; Franzen, S.; Feldheim, D. L. *Anal. Chem.* **2001**, *73*, 5758−5761. Wei, G.-T.; Liu, F.-K.; Wang, C. R. C. *Anal. Chem.* **1999**, *71*, 2085−2091.

ladium particles efficiently shorting out the polymer film. This argument is both supported by the fact that the short circuit current in the photovoltaic device geometry is relatively unaffected, but open circuit voltages are low when comparing **1a** that has no palladium nanoparticles with **1b** and **1c**. Further, the electroluminescence experiments revealed emission of light according to where the voltage is in the device.

Possible Explanation for the Palladium Affinity of PPV. As mentioned in the Introduction, there are numerous accounts of conjugated polymer synthesis involving the different types of palladium couplings.[7-11] It is also noteworthy that in many cases functional devices have been obtained. When examining the literature, however, it becomes obvious that most of these are polyarenes, such as the polyfluorenes or the polythiophenes. One notable property of the PPV backbone is the presence of a vinylene bond that is known to form a complex with palladium. We believe that this could explain why PPVs have problems with residual palladium catalyst and polyarenes do not. This fact also explains why the palladium nanoparticles are seemingly soluble. An added possibility is the effect of the end groups. While the end groups (bromine and vinyl) are not expected to have a negative influence on the electronic properties (through charge carrier trapping) the terminal vinyl groups could have a stronger affinity than the in-chain vinylene groups to palladium, and this could explain the strong binding between the palladium particles and the polymers, as in the case of **1b**, where the molecular weight is quite low. We attempted ultracentrifugation to verify this point and found that most of the polymer material deposited together with the palladium. Upon concentration of the supernatant devices could be made, and while this gave a marginal improvement on the device resistance in the case of PEDOT:PSS devices (shown in Table 1), it would seem that the conjugated polymer and the particles are intimately linked. One possible way to account for this is if the palladium in the freshly prepared polymer material is bound as complexed palladium(0) that then gradually (over time) aggregates, forms particles, and eventually reaches the nanoparticle stage we observe that are still bound to the polymer chains.

Attempts To Remove the Palladium Nanoparticles. It would seem obvious that an effective means for removal of the palladium nanoparticles from the crude polymer product is necessary before any application of the conjugated electroactive polymer material based on an electrical current can be anticipated. While there have been a few reports[24-26] on the contamination of a product with residual palladium catalyst, there has been no successful report of its removal in case of a polymer product. For small molecules[25,26] it is easier to obtain the desired product free of residual catalyst. In the case of a polymer product, however, the complete removal is difficult to envisage. The reported approach for a polymer product involved treatment with a phosphine to partly remove the residual palladium catalyst.[24] Photovoltaics and light-emitting devices based on conjugated polymer materials prepared by palladium catalysis can thus be expected to be problematic if thin films are involved (20−200 nm in thickness). Also there have been a few reports of odd solubility behavior reported where the crude polymer product is readily soluble but the dried polymer product becomes insoluble[27] or a synthetic procedure that involves Soxhlet extraction to remove traces of residual catalyst before successful application to polymer light-emitting diodes.[28] We attempted a series of microfiltration experiments, and while this had an effect on the resistance of devices, filtration did not completely solve the problem. Multiple subsequent filtrations through 2.7, 1.0, 0.45, and 0.1 μm microfilters resulted in a relatively small increase in the device resistance from 30 to 60 Ω. We further attempted to boil the polymer in a 1:1 mixture of 1,2-dichlorobenzene and triphenylphosphine and subsequently precipitated the polymer with methanol after microfiltration. This increased the device resistance to 100 Ω. While this is probably the best means of limiting the palladium nanoparticle content, we did not find any successful means of achieving complete removal of the particles. The unsuccessful procedures were treatment with activated carbon and aqua regia. The activated carbon was very successful in adsorbing both the palladium particles and the polymer. In fact, microfiltration using a 1.0 μm microfilter of a polymer/palladium nanoparticle solution in chlorobenzene that had been shaken for 1 h gave a near colorless filtrate, indicating that most of the conjugated polymer materials had been adsorbed on to the activated carbon as well. Aqua regia efficiently dissolved the palladium but, as expected, also destroyed the polymer material. The noble nature of palladium metal makes it difficult to envisage any chemical means of removing the palladium.

Consequences of Palladium Nanoparticles on Conjugated Polymer Research. Conjugated polymer materials have been studied intensely and have now made their way to commercial products. The reported synthetic procedures leading to conjugated polymer materials have been many and among these procedures palladium routes are found. There are recent reports on the synthesis of light emissive polyphenyleneethynylene polymers using a palladium route[29] and others where palladium enters in the synthetic path of the monomer but is not used in the actual polymerization step where a Gilch polymerization to the PPV has been employed.[30] Our results indicate that a palladium route can lead to palladium nanoparticles as a contaminant in the conjugated polymer product that are not easily removed. We have shown that this can have deleterious effects on electroactive devices based on the palladium nanoparticle containing conjugated polymer product. While our results may not be general to all polymer

---

[24] van Broekhoven, J. A. M. European Patent 0 283 092, 1988.

[25] Larsen, R. D.; King, A. O.; Chen, C. Y.; Corley, E. G.; Foster, B. S.; Roberts, F. E.; Yang, C.; Lieberman, D. R.; Reamer, R. A.; Tschaen, D. M.; Verhoeven, T. R.; Reider, P. J.; Lo, Y. S.; Rossano, L. T.; Brookes, A. S.; Meloni, D.; Moore, J. R.; Arnett, J. F. *J. Org. Chem.* **1994**, *59*, 6391−6394.

[26] Chen, C.; Dagneau, P.; Grabowski, E. J. J.; Oballa, R.; O'shea, P.; Prasit, P.; Robichaud, J.; Tillyer, R.; Wang, X. *J. Org. Chem.* **2003**, *68*, 2633−2638.

[27] Solomin, V. A.; Heitz, W. *Macromol. Chem. Phys.* **1994**, *195*, 303−314.

[28] Lopez, L. C.; Strohriegl, P.; Stübinger, T. *Macromol. Chem. Phys.* **2002**, *203*, 1926−1930.

[29] Pizzoferranto, R.; Berliocchi, M.; Di Carlo, A.; Lugli, P.; Venanzi, M.; Micozzi, A.; Ricci, A.; Lo Sterzo, C. *Macromolecules* **2003**, *36*, 2215−2223.

[30] Chen, Z. K.; Hoi Sim Lee, N.; Huang, W.; Xu, Y. S.; Cao, Y. *Macromolecules* **2003**, *36*, 1009−1020.

products where palladium has been employed in the synthesis, our findings suggest that it is worthwhile checking a polymer product for palladium contaminants before using them in electroactive devices or drawing conclusions based on results from physical experiments.

Conclusion

Palladium nanoparticles may influence the properties of a thin film of polymer by acting as very efficient channel for the charge carriers. If the particles span the entire height of the film, this simply results in a short circuit. Smaller particles may be almost as damaging to the performance by creating small zones where conduction preferably takes place. A simple calculation shows that even a very small amount of residual palladium (=0.01 wt %) evenly distributed in a polymer film (100 nm thick) will result in $\sim 10^6$ palladium particles with a diameter of 20 nm in an area of 1 cm^2. We have found that polymers prepared via palladium-catalyzed reactions are contaminated with palladium metal nanoparticles that cannot be removed completely. In our case this severely impaired the electrical properties of thin polymer films and limits the applicability of the polymer product for electroactive devices. The general rule of thumb should be to pay attention to the possible contamination of a polymer product with palladium particles when a palladium route is chosen. For this reason it advisable to avoid palladium in the polymerization step, as it can be very difficult to remove from the polymer product and can severely influence the electrical properties.

Acknowledgment. This work was supported by the Danish Technical Research Council (STVF). We would like to express sincere gratitude to Lotte Nielsen for the SEC measurements and Jørgen Bilde-Sørensen for technical assistance with electron microscopy.

Supporting Information Available: NMR spectra of the polymers **1a**, **1b**, and **1c**; EDX and ESCA analysis results; and an SEC trace for **1b**. This material is available free of charge via the Internet at http//:pubs.acs.org.

CM035205W