ADVANCES AND APPLICATIONS OF INHERENTLY CONDUCTIVE POLYMER TECHNOLOGIES BASED ON POLY(3,4-ETHYLENEDIOXYTHIOPHENE)

Dr. Jill Simpson*, Dr. Stephan Kirchmeyer§, Dr. Knud Reuter§
*H.C. Starck, Inc., 45 Industrial Place, Newton, MA 02461 USA, Tel (617) 630-5878, fax (617) 559-3906, Email jill.simpson@hcstarck.com; § H.C. Starck, GmbH., C/o Bayer AG, Gebaude B 202, 51368 Leverkusen, Germany

ABSTRACT

The development and recent advances in inherently conducting polymer (ICP) chemistry based on poly (3,4-ethylenedioxythiophene) (PEDT) are discussed. PEDT-based coatings can be deposited on rigid or flexible substrates via batch or roll to roll coating processes. Properties and formulations are highlighted in some relevant applications such as highly transparent conductive coatings for ESD (electrostatic discharge) protection and transparent circuitry for inorganic electroluminescent devices. Final coating properties are controlled and adjusted by careful formulation of coating ingredients, the guidelines for which will be discussed in this paper.

INTRODUCTION

A Brief Overview and History of Organic Conductors

The fundamental discoveries by Shirakawa, MacDiarmid, Heeger and coworkers of polymeric organic conductors in the 1970s marked the beginning of a completely new field. The field grew rapidly, and in 2000, their pioneering work was awarded the Nobel Prize in chemistry.[1,2] The number of publications and patents granted in the field has grown steadily over the last quarter-century, and within the last 10 years, *inherently conductive polymers* (ICPs) have developed from laboratory curiosities into mature industrial products for real commercial applications. While early versions of ICPs had drawbacks such as instability in air and poor processability, investigation of alternative polymer backbones has yielded several promising polymer types, including polypyrroles, polyanilines, and polythiophenes.

Poly(3,4-ethylenedioxythiophene) (PEDT)—a Particularly Useful ICP

A breakthrough in the area of polythiophene-based ICPs was the synthesis of polymers based on the bicyclic monomer 3,4-ethylenedioxythiophene (EDT) and its derivatives - electrochemically polymerized by Heinze *et al.* and chemically polymerized by Jonas *et al.* of the Bayer Corporate Research laboratories.[3] Poly-3,4-ethylenedioxythiophene (PEDT, or PEDOT) has a narrow HOMO-LUMO bandgap which allows the formation of a tremendously stable and highly conductive cationic “doped” state.[4] Due to these characteristics, technical use and commercialization of PEDT quickly followed; today ICPs based on PEDT are commercially available in multi-ton quantities.

PEDT plays an important commercial role in antistatic and conductive coatings, electronic components, and displays. In particular, widespread applications have been commercialized using the humidity-independent conducting properties of both the PEDT complex with polystyrene sulfonic acid (PEDT:PSS) and the *in situ*-polymerized layers of the EDT monomer, hereinafter referred to as *in situ*-PEDT.[5] Antistatic coating applications for PEDT:PSS include photographic films,[6] electronics packaging, CRT screens and LCD polarizer films. Conductive films of PEDT:PSS are found in inorganic electroluminescent devices and all-organic field effect transistors, and PEDT:PSS layers function as the hole-injection layer in polymeric organic light-emitting diodes and polymer photovoltaic cells. *In situ*-PEDT is also well-established in industry; it is used as a polymeric cathode material for solid aluminium, tantalum, and niobium capacitors, and as a conductive template for Cu-through-hole plating of printed wiring boards.

THE CHEMISTRY OF PEDT

In-situ PEDT Formed by Oxidative Polymerization

The physical characteristics of an *in situ*-polymerized PEDT film are affected by a variety of factors. Variables in the synthetic method used to manufacture PEDT will affect the resulting polymer morphology, crystallinity, doping level, conductivity, molecular weight, processability, etc. In general, the more uniform, or crystalline, a PEDT film is, the higher its conductivity. The reaction of EDT with iron(III) *p*-toluenesulfonate is summarized in Figure 1. The overall polymerization reaction can be separated into two principal steps: (1) oxidative polymerization of the monomer to the neutral polythiophene, and (2) oxidative doping of the neutral polymer to the conductive polycation.

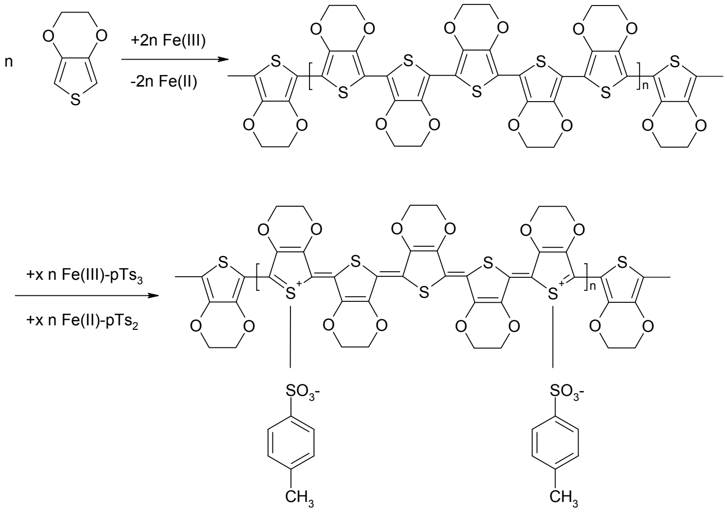


Figure 1. Oxidation of 3,4-ethylenedioxythiophene with iron(III) *p*-toluenesulfonate. Doping level of resulting polymer is x ~ 3. Overall stoichiometry is 1 mol EDT : 2.3 mol iron(III) *p*-toluenesulfonate (pTs). Commonly used solvents are ethanol, *n*-butanol, etc.

The PEDT:PSS-Complex Formed by Template Polymerization with PSSA

Since *in situ*-polymerized PEDT polymers are quite insoluble in most commonly-used solvents, *in situ*-PEDT cannot be easily made into a processable, coatable solution. However, a more industrially useful form of conductive PEDT can be made by aqueous oxidative polymerization of the EDT monomer in the presence of a template polymer, usually polystyrene sulfonic acid (PSS or PSSA). PSS is a commercially available water-soluble polymer and can thus serve as a good dispersant for aqueous PEDT. Polymerization with the oxidant sodium peroxodisulfate yields a PEDT:PSS-complex in its conductive, cationic form (Figure 2).

The PSS in the complex has two functions. First, it functions as the charge balancing counter ion to the PEDT.[6] Second, it helps to disperse the PEDT segments in the surrounding water. Although the resulting PEDT:PSS complex is not truly water soluble, the reaction forms a stable, easy-to-process, deep blue dispersion of nanometer-sized polymer gel particles.

Two key factors are important for understanding the nature of the PEDT:PSS-complex. First, the PEDT segments formed during polymerization are most likely oligomeric rather than polymeric. It has not been possible to directly observe high molecular weight PEDT polymers, and analyses of various PEDT-containing polymers *via* MALDI-TOF mass spectroscopy strongly support this assumption. Several measurements with PEDT:PSS or with substituted PEDT derivatives, including neutral PEDT molecules, indicate that the molecular weights of the individual PEDT molecules do not exceed 1000 to 2500 Dalton, or about 6 to 18 repeating units.[7] Second, the PEDT:PSS-complex has high stability. Inganäs *et al.* demonstrated that the ionic species $PEDT^+$ and PSS^- could not be separated by standard capillary electrophoresis methods.[8]

Structure of the PEDT:PSS Complex

The above evidence, taken together, indicates that it is therefore appropriate to draw a structural model for the secondary and tertiary structures of PEDT:PSS as shown in Figure 3. In this model, oligomeric PEDT segments are tightly, electrostatically attached to PSS chains of much higher molecular weight. The high conductivity of PEDT:PSS can be attributed to stacked arrangements of the PEDT chains within a larger, tangled structure of loosely crosslinked, highly water-swollen PSS gel particles in films. These particles consist roughly of 90 to 95 % water. The maximum solids content achievable, while maintaining a stable dispersion, depends on the PEDT to PSS ratio and increases with increasing PSS content, but is generally on the order of 10% or less. The PEDT:PSS gel particles have excellent film forming properties and are easily processable into thin coatings on a variety of substrates. This coating processability led to the widespread availability of PEDT:PSS as a commercially useful material for the production of pH- and humidity-independent, highly transparent conductive polymer coatings.[9]

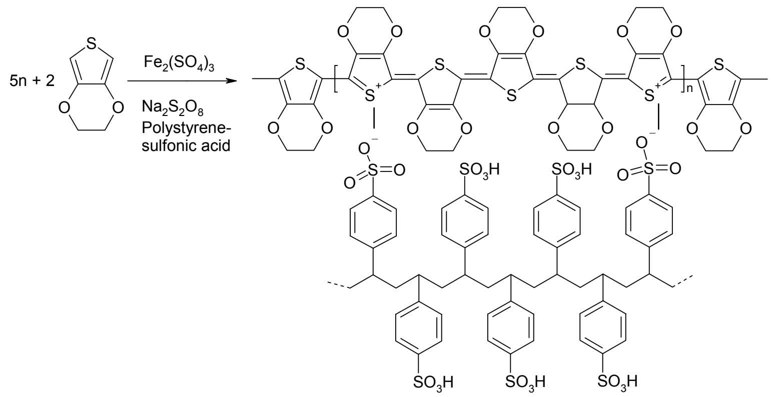


Figure 2. Synthesis of PEDT:PSS

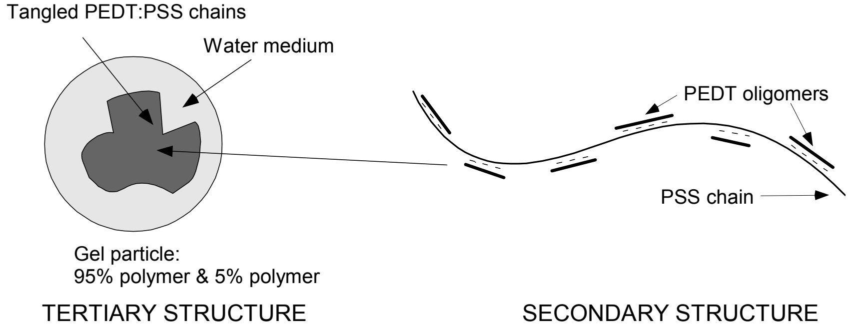


Figure 3. Secondary and tertiary structure of PEDT:PSS

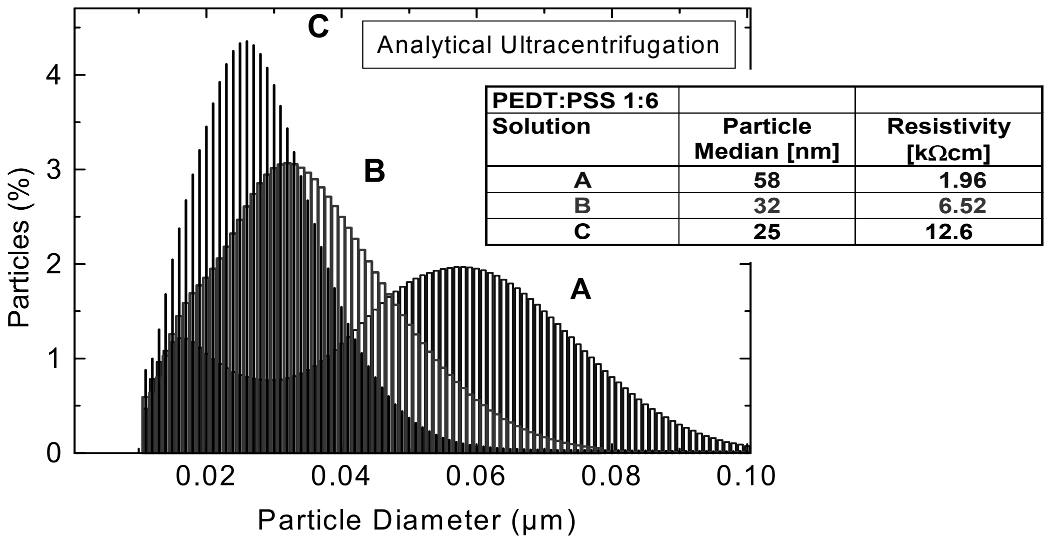
Properties of PEDT:PSS

Several typical properties of PEDT:PSS polymers are summarized in Table 1. Antistatic and conductive grades of PEDT:PSS have relatively low PSS-contents, and therefore higher conductivity values. In contrast, PEDT:PSS grades designed for hole-injection in polymer OLEDs and other passive matrix displays have larger PSS contents, smaller particles, and lower conductivities in order to prevent cross-talk in multi-pixel devices. Increasing the PSS content logically reduces the electrical conductivity by diluting the conductive PEDT in the material.

Table 1. Typical PEDT:PSS grades and their characteristics

PEDT:PSS Ratio	Solids content, approximate (%)	Electrical conductivity, approximate (S/cm)	Typical application
1 : 2.5 plus 5% bw DMSO	1.3	Up to 500	Conductive coatings
1 : 2.5	1.3	10	Conductive coatings
1 : 2.5	1.3	1	Antistatics
1 : 6	1.5	10^{-3}	OLEDs
1 : 20	3	10^{-5}	Passive Matrix Displays

Particle size, which can be varied by applying different high pressure shear rates to the PEDT:PSS dispersion during manufacture, is also tightly linked to film conductivity: the smaller the particles, the lower the conductivity of the PEDT:PSS in the final, dried film. This is demonstrated in Figure 4. Particle boundaries between the dried gel particles in a film contribute significantly to the overall resistivity of the film. The highest conductivities are achieved, therefore, when the particles are largest, *i.e.* when the total number of particle boundaries in a given volume or area is minimized. Alternatively, the PEDT:PSS film conductivity is enhanced when there is significant intermingling of individual gel particles, which reduces the effective number or “size” of the particle boundaries.



PEDT:PSS 1:6 Solution	Particle Median [nm]	Resistivity [kΩcm]
A	58	1.96
B	32	6.52
C	25	12.6

Figure 4. Relationship between particle size and resistivity, assuming a constant 1.6 ratio of PEDT to PSS.

The PEDT:PSS complex has a deep ink-blue color. However, because the PEDT:PSS dispersions have very low solids contents, and because the material is therefore applied in very thin films, highly transparent coatings can be readily made. At normal layer thicknesses, usually of about 200 nm or less based on PEDT:PSS only, the total amount of PEDT:PSS on the substrate surface is small, and so the visible light transmission through the film is quite high, at about 85% or more, as shown in Figure 5.

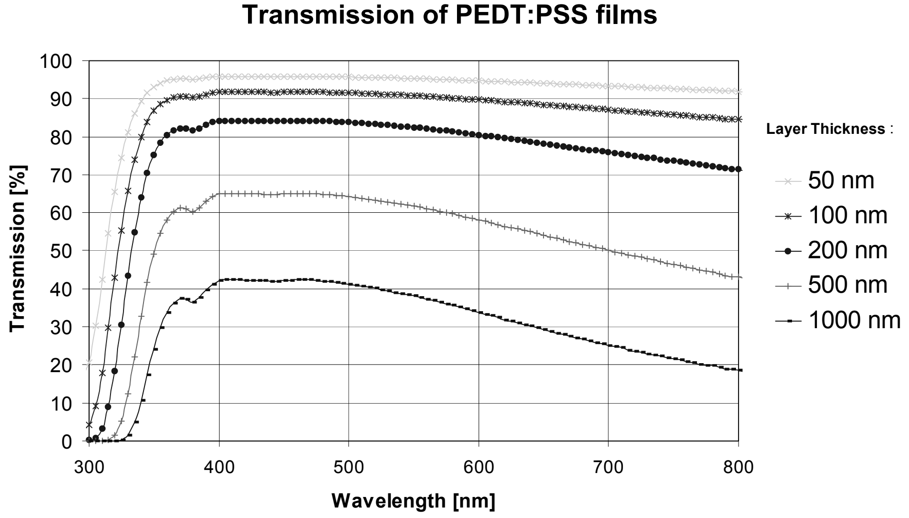


Figure 5. Transmission spectrum of PEDT:PSS films of varying layer thicknesses, taken on Perkin Elmer Lambda 900 with integrating sphere, using a 200-nm thick layer of PEDT:PSS on quartz substrate. The transmission data were taken in air and not corrected for reflection losses.

APPLICATIONS FOR PEDT:PSS

PEDT Coating Formulations

Applications using *in-situ* polymerized PEDT must be distinguished from applications that utilize the PEDT:PSS complex. Since *in situ*-PEDT films are formed *via* a chemical reaction as shown in Figure 1, the process must be directly controlled during polymer formation. For example, kinetic parameters for *in situ*-PEDT film formation can be controlled by addition of components, such as amines, that modify the reaction rate, and hence the final film properties.[10] Furthermore, iron salts from the spent oxidant must be physically removed from the film after polymerization by washing. In general, *in situ*-PEDT is used to obtain the highest conductivity. PEDT-films with conductivities of 500 to 700 S/cm are easily attainable, and conductivities of 1000 S/cm and higher can be obtained with strict control of processing conditions. One caveat is that high conductivity *in situ*-PEDT films are not generally highly transparent.

In contrast, the PEDT:PSS-complex is a “prefabricated” polymer, so film properties are instead adjusted by “formulation”—the addition of film-forming binders, surfactants, wetting agents, adhesion promoters, etc., to the coating mixture. The conductivity of unformulated PEDT:PSS layers is between 1 and 10 S/cm. However, if desired, conductivity can usually be increased upon formulation by as much as 1 to 2 orders of magnitude. This is clearly in contrast to what one might expect—that the addition of non-conductive components would lower the overall conductivity! Of course, formulation can also be used to adjust conductivities to lower values, like those required for the production of antistatic or ESD protection coatings, by the addition of large amounts of non-conductive components such as inert binders. In general, PEDT:PSS can be used achieve either low or high surface resistivities—ranging from 1.0 x 10^2 ohms to <1.0 x 10^9 ohms—depending on coating formulation and application method.

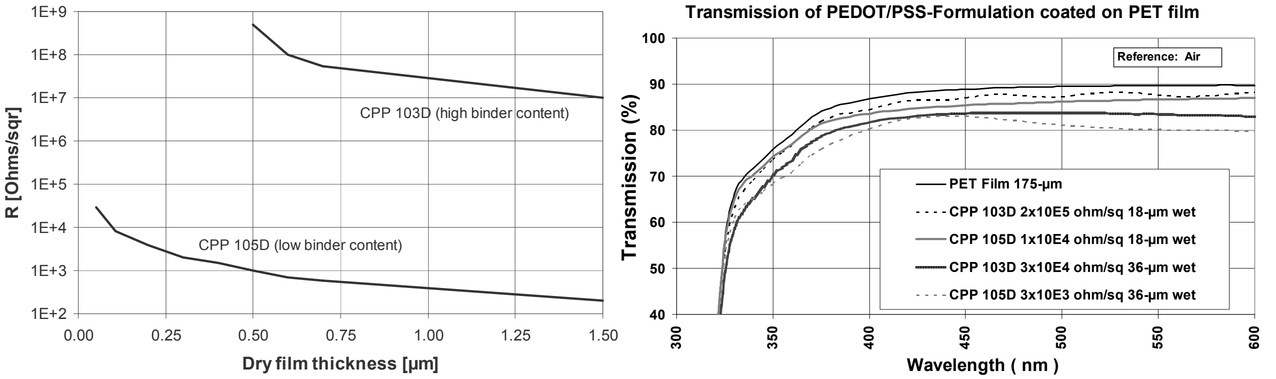


Figure 6. A comparison of two coating formulations—CPP103D with high binder/low PEDT:PSS content and CPP105D with low binder/high PEDT:PSS content.[11] The comparison therefore shows the relationship between thickness of a PEDT:PSS-based film and both its conductivity and its transmission, and how these properties also depend on coating formulation. On the left, surface resistance versus dry film thickness is shown for the two different formulations. The surface resistance of the formulation CPP105D is lower for all thicknesses due to its higher relative PEDT:PSS content, but for both formulations, the surface resistance goes down with increasing film thickness. On the right is shown the relationship between transmission and coating formulation. The same two coating formulations are demonstrated for two different wet film thicknesses, and the results show that the overall transmission is reduced by increasing the amount of PEDT:PSS in the coating—*i.e.* by using a formulation with low binder content like CPP105D or by using a thicker coating.

Coating conductivity can also be adjusted by varying the coating layer thickness. In general, as one increases the PEDT-coating layer thickness, the conductivity is increased. However, as discussed in the previous section, the transmission of PEDT-based films decreases with increasing coating thickness and PEDT-content. Therefore, a balance must be struck between the desired coating conductivity, layer thickness, and transparency properties. See Figure 6 for a comparison of the conductivities and transmission of two typical coating formulations applied at different thicknesses, and see Table 2 for an illustration of how thickness, conductivity, and transparency are linked.

Table 2: Increasing one characteristic of a PEDT:PSS-based coating will have an effect on other coating properties.

		Affected Property (↑ or ↓)		
		Thickness	Transparency	Conductivity
Increased (↑) property	Thickness		↓	↑
	Transparency	↓		↓
	Conductivity	↑	↓	

Common formulation components and their effects on PEDT:PSS films are as follows:

Low boiling solvents such as alcohols and some low boiling carbonyl-containing solvents may be added to lower the surface tension of the PEDT:PSS dispersion, thereby increasing the wetting of substrates. These additives are especially needed when plastic substrates such as polyester (PET), polycarbonate (PC), or polyethylene (PE) are to be coated with the aqueous PEDT:PSS dispersion.

Surface active components such as non-ionic surfactants may be used for the same purpose as low boiling solvents. Because the solids contents of the aqueous PEDT:PSS dispersions are usually rather low (between 1.5 and 4%), and because non-volatile additives will accumulate in the dried films, these additives are effective at extremely low loading levels. For example, a surfactant that has been added to the PEDT:PSS coating formulation at a 1% loading level will make up as much as 30% of the final, dried film.

Polymeric binders such as waterborne polyesters and polyurethanes are often used to improve the adhesive and mechanical properties of PEDT-based films. Especially in cases where plastic substrates are coated by PEDT:PSS and subsequently mechanically treated after coating, such as by thermoforming, addition of a binder to the PEDT:PSS can help to maintain the overall conductivity by maintaining particle-particle connectivity. Choice of binder varies with the targeted properties of the final film. If, for example, an end-user desires a coating that is resistant to a particular solvent and well-adherent to PC, then a binder designed specifically for solvent-resistant coatings on PC should be chosen.

Polymeric binders can also be used as a nonconductive matrix material for adjusting overall surface resistivity of a film. For example, if an antistatic coating surface resistivity of 10^6 Ohms/square or higher is targeted, a high percentage of binder is employed. For lower surface resistivities, lower binder percentages are used. See Figure 6 for a comparison of the surface resistivities of two different formulations—one with high binder content (CPP 103D) and one with low binder content (CPP 105D).

Silanes and tetraalkylorthosilicates are often used to increase the adhesion to the underlying substrate or to increase the hardness and wear resistance of the conducting film.

A very important class of additives for formulations is ***high boiling solvents*** and other ***polar compounds***. Particularly useful are amides such as N-methylpyrrolidone and dimethylformamide, polyhydroxy compounds like ethylene glycol and sugar alcohols,[12] and sulfoxides like dimethylsulfoxide. These solvents, often called “secondary dopants,”[13] are used in small amounts to increase the conductivity of the final, dried film. The effects of these additives are independent of whether they remain in the film after drying or not. The mechanism of this conductivity enhancement has been discussed in depth by Pettersen *et al.* and others.[14] The interpretation favored by these authors is that polar solvents at least partly dissolve the PEDT-stacks in the PEDT:PSS complex, thereby creating an opportunity for a favorable morphological rearrangement and clustering of gel particles.[15] The rearrangement leads to a decreased resistance between dried gel particles, thus increasing the overall conductivity of the film.

Application methods. Application of PEDT-based coatings to substrates can be accomplished by a variety of methods. For small and irregularly-shaped parts, spray-coating or dip-coating is often preferred. For larger substrates such as plastic sheets or wide-web plastic rolls, other application methods are convenient, such as gravure printing, roller coating, etc. For the deposition of patterned PEDT films, ink-jet, screen, or nozzle printing can be used. In all cases, care must be taken in design of the coating formulation so that the mixture is compatible with the desired application method. As with all water-based coating formulations, adhesion to plastic substrates can be improved by corona- or plasma-pretreatment of the substrate.

Curing & drying of PEDT coatings. Unlike traditional antistatic coatings, the PEDT-based coatings are normally physically dried in an oven at temperatures between 80 to 200 °C. The drying time depends on coating thickness, temperature and air humidity, and should be determined by appropriate application tests.

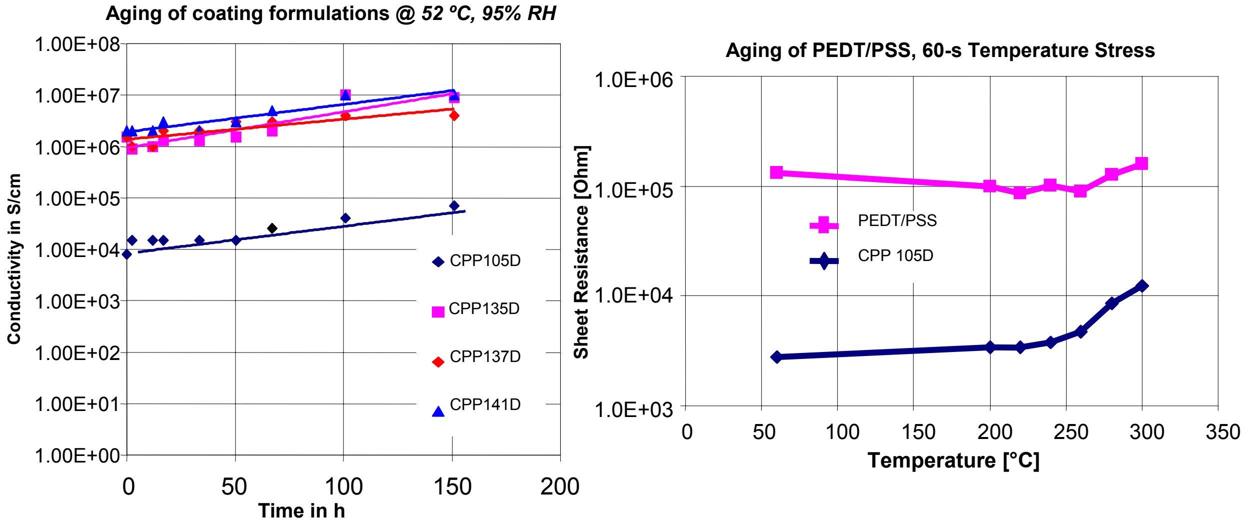


Figure 7. On the left is aging and temperature stability data for selected PEDT:PSS-based coating formulations.[16] On the right is temperature stability of neat PEDT:PSS and of coating formulation CPP 105D. The temperature stress experiment was performed by subjecting the coatings to rapid temperature increases of 20 °C over 60 seconds.

As shown in Figure 7, stability of PEDT-based coatings is in general quite high, both in terms of absolute temperature stability[17] of the PEDT:PSS and in terms of aging of different coating formulations. For most cases, the aging stability of PEDT:PSS-based coating formulations can be considered stable within one order of magnitude over several hundred hours for even high temperature and high humidity environments. As long as the environmental temperature that a coating is subjected to is kept below the absolute temperature stability of the PEDT:PSS, all the other ingredients in the formulation, and the substrate, then degradation of a coating's properties can usually at least partially be attributed to coating delamination, or disruption of the conductive network. If for example, a "soft" binder is used in the coating, swelling of the film can occur, leading to inhomogeneities in the coating that disrupt the particle-to-particle conductive pathways.

SOME COMMERCIAL APPLICATION EXAMPLES

Antistatic Coatings

Typical requirements for antistatic layers are:

- humidity-independent surface resistance of 10^5 to 10^9 Ω/square,
- transparent, practically colourless and haze-free appearance,
- good adhesion to the substrate, and
- hardness of the coating.

The first commercial-scale use of PEDT:PSS was for roll-to-roll deposition of an antistatic layer onto PET during photographic film production in order to avoid unwanted, stray electrostatic discharges within the photoactive layers during film processing. The use of PEDT:PSS as the conductive ingredient in the antistatic layer proved particularly advantageous because of its high conductivity, low-colour, stability, processability and moisture independent antistatic effect.[18]

In a second commercial antistatic application, PEDT:PSS was used as the conductive ingredient in an outer surface antistatic layer on cathode ray tubes (CRT) to avoid dust contamination during manufacture and use (Figure 8). In addition to the same advantages described above, the PEDT:PSS layer was found to enhance optical contrast in the displays. Formulations for PEDT:PSS antistatic layers for optical applications such as this require fine polymer gel particle size distributions, sufficient coating hardness, good adhesion to glass, and a surface resistance of about 10^6 Ω/square.

The other uses of PEDT:PSS for antistatic layers are numerous[13,14] and include antistatic gloves,[19] carrier tapes, displays and video display panels,[20] textiles,[21] antistatic release films,[22] protective films,[23] recording tapes,[24] and polarizers.[25]

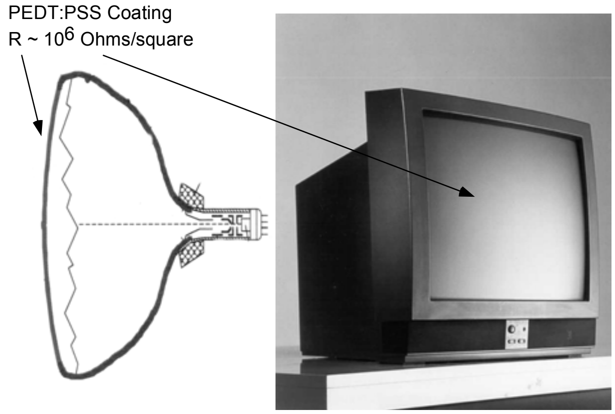


Figure 8: PEDT:PSS as an antistatic coating for glass cathode ray tube displays to avoid dust attraction during manufacturing and use. A typical coating formulation for this application is required to be hard and scratch resistant, so the coating mixture would normally include a siloxane binder system.

Electrically Conducting Coatings

Conductive coatings are used to conduct the current needed for the operation of electronic devices, and in most cases the current density required for device operation is several orders of magnitude higher than that required for protection against antistatic discharges. Therefore, in these applications it is usually necessary to obtain layers with the maximum conductivity possible. Over the last decade, great progress has been made in efforts to synthesize higher conductivity versions of PEDT:PSS as shown in the trend line on the right side of Figure 9. Today, PEDT:PSS dispersions with inherent conductivities as high as about 600 S/cm are attainable. For comparison, the average conductivity of an *in situ*- PEDT layer is about 1000 S/cm.

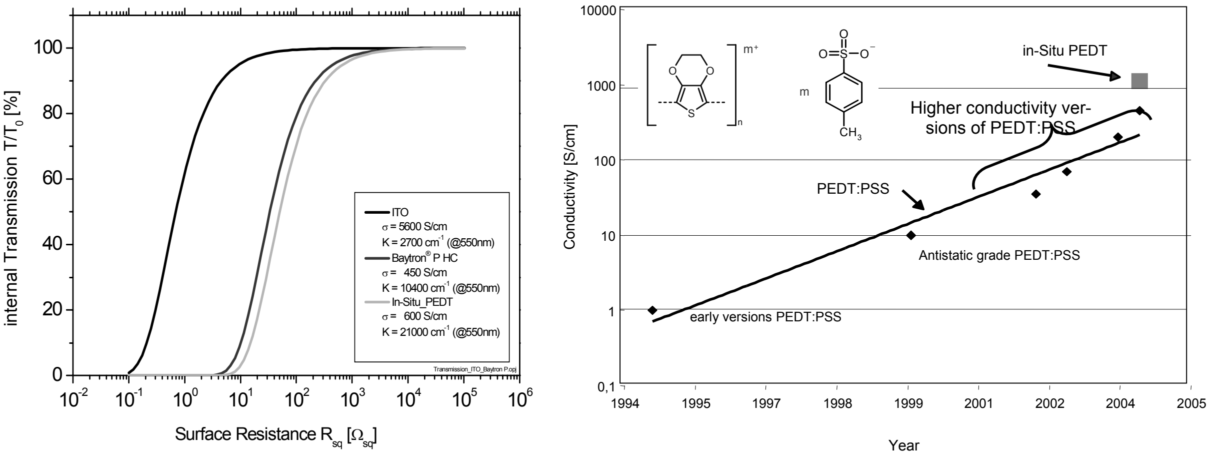


Figure 9. The left graph shows the relationship between conductivity and transparency of one version of PEDT:PSS (BAYTRON® P HC), compared to ITO and to *in situ*-PEDT. The figure on the right shows the progress over the last decade in increasing the inherent conductivity of PEDT:PSS dispersions. As of 2005, PEDT:PSS dispersions can be manufactured with conductivities as high as about 600 S/cm.

Often transparent conducting layers are required for a particular device configuration, and today PEDT:PSS types are available with sufficient conductivity to perform this function. For any transparent conductor, including for the industry standard indium-tin-oxide (ITO), the thickness is limited by the specific absorption of the conductor and the required transparency of the conducting layer. In PEDT-based films, as a first approximation the transparency is determined by calculating the absorption of PEDT in the film, independent of whether the film was obtained from *in situ*-generated PEDT, from PEDT:PSS, or from a formulation containing PEDT:PSS. On the left side of Figure 9, transmission is depicted *versus* surface resistance for ITO, a highly conductive PEDT:PSS grade (BAYTRON® P HC), and *in situ*-polymerized PEDT layers. Surface resistance is adjusted by varying the layer thicknesses; consequently, a compromise must be made, near the upper part of the curves, between high transmission values and low surface resistances. The inset on the left graph of Figure 9 indicates the specific conductivities and absorption coefficients (at 550 nm) of the three layers compared in this study.

PEDT:PSS as a Transparent Conductor in Electroluminescent Devices

Inorganic electroluminescent (EL-) devices comprise a composite active layer of a zinc sulfide emitter and a dielectric such as barium titanate sandwiched between two conducting layers, one of which must be transparent. When an AC voltage of approximately 100 V/400 Hz is applied, the zinc sulfide emits light, the hue of which can be tuned by the addition of appropriate doping agents. Figure 10 shows a schematic of the layered structure of typical EL device in which the transparent electrode is made with PEDT:PSS.

Due to the relatively high voltage used in typical EL devices, the specific resistance of the transparent conductor can be relatively low, at around 10^3 Ω/square. Therefore it is possible to replace the normally-used ITO by a conducting polymer[26] such as PEDT:PSS. Even though the polymer has a lower specific conductance compared to ITO, all of the layers in the polymer-based device can be applied by printing techniques such as silkscreen printing. ITO, on the other hand, must usually be applied by costly sputtering deposition techniques.

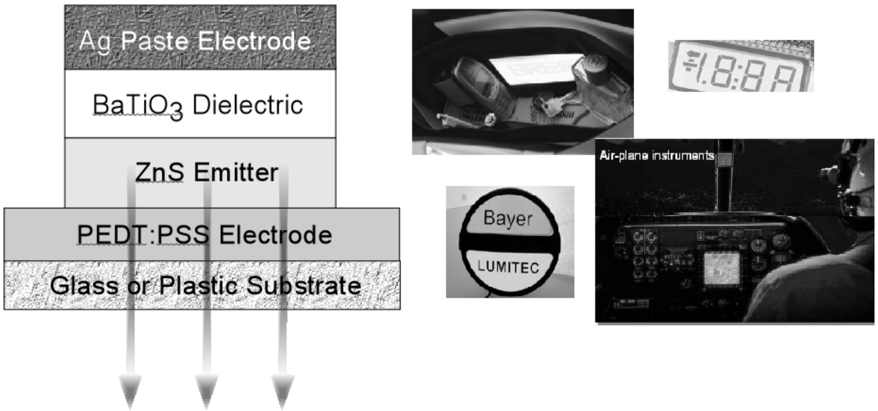


Figure 10. Schematic structure of an inorganic electroluminescent device with a transparent electrode made from a printing paste formulation of PEDT/PSS (screen printing technique) and examples of devices using this technology. [Photos courtesy of Bayer MaterialScience AG, Leverkusen, Germany, Lumitec Ltd., Gais, Switzerland, and BREE Collection GmbH & Co. KG, Germany]

Besides lower process costs, an additional technical advantage to the use of a PEDT:PSS-based printing paste for the transparent conductor is the flexibility of the contact layer. ITO is a brittle, inorganic material not ideally suited to destruction-free thermal deformation. In contrast, devices fabricated with transparent, conductive PEDT:PSS electrodes can be three-dimensionally[27] thermoformed after construction of the EL elements.

SUMMARY

Due its commercial availability on a large scale, PEDT has already found its way into myriad commercial applications, most of which capitalize upon the ability to create transparent, yet conductive, coatings with PEDT. The use of PEDT is expected to continue to grow in commercial applications as new versions of PEDT:PSS dispersions and coating formulations are developed, and as new applications for ICPs are identified.

ACKNOWLEDGEMENTS

The authors express thanks to Dr. Klaus Wussow, Dr. Friedrich Jonas, Mr. Udo Guntermann, Dr. Wilfried Loevenich (Application Technology PEDT), Dr. Andreas Elschner (Device Physics), and Dr. Alexander Karbach (X-ray, AFM).

REFERENCES

---

1 (a) C. K. Chiang, C. R. Fincher, Y. W. Park, A. J. Heeger, H. Shirakawa, E. J. Louis, S. C. Gau and A. G. MacDiarmid, *Phys. Rev. Lett.* 1977, **39**(17), 1098; (b) H. Shirakawa, E. J. Louis, A. G. MacDiarmid, C. K. Chiang and A. J. Heeger, *J. Chem. Soc. Chem. Commun.* **1977**(16), 578; (c) T. Ito, H. Shirakawa and S. Ikeda, *J. Polym. Sci. Polym. Chem. Ed.* **1974**(12), 11; (d) H. Shirakawa, *Angew. Chem. Int. Ed.* 2001, **40**(14), 2575.

2 (*a*) A. J. Heeger, *Angew. Chem., Int. Ed.* 2001, **40**(14), 2591; (*b*) A. J. Heeger, *Synth. Met.* 2001 (Volume Date 2002), **125**(1), 23.

3 (a) F. Jonas, G. Heywang, W. Schmidtberg, J. Heinze and M. Dietrich, EP 339 340 (Bayer AG), Prior.: 1988-04-22; (b) G. Heywang and F. Jonas, *Adv. Mater.* 1992, **4**(2), 117.

4 Q. Pei, G. Zuccarello, M. Ahlskog and O. Inganäs, *Polymer* 1994, **35**(7), 1347.

5 S. Kirchmeyer, K. Reuter, *J. Mater. Chem.* 2005, **15**, 2077.

6 F. Jonas and W. Krafft, EP 440 957 (Bayer AG), Prior.: 1990-02-08.

7 (a) F. Jonas, L. Groenendaal and J. Pausch, unpublished results; (b) K. Reuter, A. Karbach, H. Ritter and N. Wrubbel, EP 1 440 974 A2 (Bayer AG), Prior.: 2003-01-21.

8 S. Ghosh and O. Inganäs, *Synth. Met.* 1999, **101**(1-3), 413.

9 F. Jonas and G. Heywang, *Electrochim. Acta* 1994, **39**(8/9), 1345.

10 A. G. J. Staring and D. Braun, WO 96 08047 (Philips Electronics N. V.), Prior.:1994- 09-06 .

11 The approximate compositions by weight of formulations use in this study are: CPP103D – 0.3% PEDT:PSS, 25.6% water, 0.1% dimethylaminoethanol, 38.8% Alberdingk-Boley binder U710, 9% N-methylpyrrolidone, 0.3% Silquest® A 187 (GE Silicones), 25.6% isopropanol, and 0.3% Dynol™ 604 (Air Products); CPP 105D – 0.6% PEDT:PSS, 42.2% water, 2.6% N-methylpyrrolidone, 0.9% Silquest® A 187 (GE Silicones), 53.3% isopropanol, and 0.3% Dynol™ 604 (Air Products).

12 (a) F. Jonas, A. Karbach, B. Muys, E. van Thillo, R. Wehrmann, A. Elschner and R. Dujardin, EP 686 662 (Bayer AG), Prior.: 1994-05-06/1995-03-03; (b) H. J. Snaith, H. Kenrick, M. Chiesa, R. H. Friend, *Polymer* 2005, **46**, 2573; (c) S. L. Lai, M. Y. Chan, M. K. Fung, C. S. Lee, S. T. Lee, *Mater. Sci. Eng. B* 2003, **104**, 26.

13 B. D. Martin, N. Nikolov, S. K. Pollack, A. Saprigin, R. Shashidar, F. Zhang and P. A. Heiney, *Synth. Met.* 2004, **142** (1-3), 187

14 (a) L. A. A. Pettersson, S. Ghosh and O. Inganäs, *Org. Electronics* 2002, **3**(3-4), 143; (b) S. K. M. Jönsson, J. Birgerson, X. Crispin, G. Greczynski, W. Osikowicz, A. W. Denier van der Gon, W. R. Salaneck and M. Fahlman, *Synth. Met.* 2003, **139**(1), 1; (c) J. Ouyang, C.-W. Chu, F.-C. Chen, Q. Xu, Y. Yang, *Adv. Funct. Mater.* 2005, **15**, 203.

15 (a) J. Ouyang, Q. Xu, C.-W. Chu, Y. Yang, G. Li and J. Shinar, *Polymer* 2004, **45**(25), 8443; (b) S. Timpanaro, M. Kemerink, F. J. Touwslager, M. M. De Kok and S. Schrader, *Chem. Phys. Lett.* 2004, **394**(4-6), 339; (c) J. Huang, P. F. Miller, J. S. Wilson, A. J. deMello, J. C. deMello, D. D. C. Bradley, *Adv. Funct. Mater.* 2005, **15**, 290.

16 The approximate compositions by weight of the formulations used in this study are as follows: (a) CPP 105D – see endnote 11; (b) CPP 135D – 0.3% PEDT:PSS, 44.9% water, 0.1% dimethylaminoethanol, 20.2% NeoRez® R986 (NeoResins), 0.2% Silquest® A 187 (GE Silicones), 30.3% isopropanol, 3.9% N-methylpyrrolidone, and 0.1% Dynol™ 604 (Air Products); (c) CPP 137D – 0.3% PEDT:PSS, 44.9% water, 0.1% dimethylaminoethanol, 20.2% Gabusen® ES 210 (Nagase ChemteX), 0.2% Silquest® A 187 (GE Silicones), 30.3% isopropanol, 3.9% N-methylpyrrolidone, and 0.1% Dynol™ 604; (d) CPP 141D – 0.7% PEDOT:PSS, 52% water, 0.2% dimethylamino-ethanol, 31.4% NeoRez® R986 (NeoResins), 10.5% Eastek® 1200-02-30% (Eastman Chemical), 2% isopropanol, 3.1% N-methylpyrrolidone, and 0.1% DynolTM 604 (Air Products).

17 J. Huang, P. F. Miller, J. C. deMello, A. J. deMello, D. D. C. Bradley, *Synth. Met.* 2003, **139**, 569.

18 (a) F. Jonas, W. Krafft and B. Muys, *Macromol. Symp.* 1995, **100**, 169; (b) F. Jonas and J. T. Morrison, *Synth. Met.* 1997, **85**(1-3), 1397; (c) F. Jonas and K. Lerch, *Kunststoffe* 1997, **87**(10), 1401.

19 A. Thiess, *Deutsche Gebrauchsmusterschrift* (2001), DE 20021226 U1, Prior.: 2001-04-19.

20 (a) O. Hotta, S. Soga and N. Sonoda, JP 02129284 (Matsushita Electric Ind. Co.), Prior.: 1988-11-08; (b) S. Y. Yoon, C. H. Lee and H. S. Son, KR 2000 009403 (Orion Electric Co.), Prior.: 1998-07-24; (c) H. Tong, J. Hu, CN 1 171 617 A (Zhonghua Kinescope Co.), Prior.: 1996-07-23.

21 G. Hardtke and H. Fuchs, *TECHNOMER '99, 16th Fachtagung über Verarbeitung und Anwendung von Polymeren,* 1999, Chemnitz, Germany; CAN 137: 80211.

22 (a) T. Kawashima and T. Sekiya, JP 2002 241613 A2 (Sony Chemical Corp.), Prior.: 2002-08-28; (b) T. Kawashima and T. Sekiya, JP 2003 251756 A2 (Sony Chemical Corp.), Prior.: 2003-09-09.

23 Y. Morimoto, JP 2000 026817 A2 (Teijin Ltd.), Prior.: 1998-07-14.

24 F. Nittel, H. Randolph and W. Himmelmann, EP 554 588 (Agfa AG), Prior.: 1993-12-23.

25 H. Shinohara, JP 2003 246874 A2 (HS Planning Y. K.), Prior.: 2002-02-26.

26 (a) H. Andriessen, EP 1 231 251 A1 (Agfa-Gevaert), Prior.: 2002-08-14; (b) A. Saito, JP 2002 124391 A2 (Seiko Precision Inc.), Prior.:2000-08-08.

27 E. Enz, WO 2003 037039 A1 (Lumitec AG), Prior.: 2001-10-24.