Why Does the Electrical Conductivity in PEDOT:PSS Decrease with PSS Content? A Study Combining Thermoelectric Measurements with Impedance Spectroscopy

Thomas Stöcker, Anna Köhler, Ralf Moos

1Department of Functional Materials, University of Bayreuth, 95440 Bayreuth, Germany
2Experimental Physics II, Department of Physics, and Bayreuth Institute of Macromolecular Science, University of Bayreuth, 95440 Bayreuth, Germany

Correspondence to: T. Stöcker (E-mail: Functional.Materials@Uni-Bayreuth.de)

Received 20 February 2012; revised 11 April 2012; accepted 11 April 2012; published online 14 May 2012
DOI: 10.1002/polb.23089

ABSTRACT: We have investigated the electrical transport properties of poly(3,4-ethylenedioxythiophene)/poly(4-styrenesulfonate) (PEDOT:PSS) with PEDOT-to-PSS ratios from 1:1 to 1:30. By combining impedance spectroscopy with thermoelectric measurements, we are able to independently determine the variation of electrical conductivity and charge carrier density with PSS content. We find the charge carrier density to be independent of the PSS content. Using a generalized effective media theory, we show that the electrical conductivity in PEDOT:PSS can be understood as percolation between sites of highly conducting PEDOT:PSS complexes with a conductivity of 2.3 (S cm⁻¹) in a matrix of excess PSS with a low conductivity of 10⁻³ (S cm⁻¹). In addition to the transport properties, the thermoelectric power factors and Seebeck coefficients have been determined. © 2012 Wiley Periodicals, Inc. J Polym Sci Part B: Polym Phys 50: 976–983, 2012

KEYWORDS: conducting polymers; charge carrier mobility; electrolyte; organic semiconductors; phase separation; Seebeck coefficient; thermal properties; thermopower

INTRODUCTION Conducting polymers have attracted much attention in the field of electronics as their electronic, optical, and mechanical properties can be tuned relatively easily by synthesis or processing methods. A particularly widely used highly conductive p-type polymer is poly(3,4-ethylenedioxythiophene) (PEDOT). Although it is not soluble by itself, it can be embedded in poly(4-styrenesulfonic acid) (PSS) using the so-called Baytron-P process. In this process, PEDOT is doped with PSS resulting in the formation of a water-based PEDOT:PSS complex. It consists of a PSS chain to which PEDOT oligomers adhere and that coils up to form a tertiary structure. In water, this complex yields a stable, deep blue microdispersion that allows for spin-coating of thin, optically transparent, conductive films. This property has resulted in considerable industrial interest.

Although the addition of PSS brings an enhanced processability, this comes at the expense of a decreased electrical conductivity. For example, PEDOT:PSS ratios ranging from 1:2.5 to 1:20 imply conductivities in the range from 1 to 10⁻⁵ S cm⁻¹, respectively. The highly conductive materials are particularly suitable for applications as antistatic-coatings, whereas low conductivities are appropriate for the realization of passive matrix displays. For the wide-spread use as a hole-transport layer in organic light emitting diodes, conductivities in the range of 10⁻³ S cm⁻¹, corresponding to a PEDOT:PSS ratio of 1:6 have been found most appropriate. The electrical conductivity of PEDOT:PSS depends not only on the content of PSS but it can also be tuned by processing conditions such as the use of particular solvents.

Despite the high industrial relevance, the mechanism of charge transport in PEDOT:PSS is only partly understood. Different effects have been suggested to account for the dependence of the electrical conductivity on additional processing solvents such as dimethyl sulfoxide, sorbitol, or ethylene glycol. These include dielectric screening due to the solvent, conformational changes of the PEDOT chain or morphological changes. Spin-cast films of PEDOT:PSS are considered to consist of a phase-segregated material consisting of about 25 nm wide lentil-shaped PEDOT:PSS grains surrounded by a nanometer-thick shell formed by PSS. The resulting conductivity is therefore strongly dependent on variations in this morphology. For example, temperature-dependent conductivity measurements demonstrate a high in-plane conductivity consistent with variable-range hopping, whereas the conductivity in the normal direction is strongly reduced and agrees with nearest neighbor hopping. Solvent treatment is considered to change the lateral charge motion from a three-dimensional (3D) to a quasi 1D variable range hopping behavior.
One difficulty in assessing the mechanism of charge transport and its dependence on morphological or processing parameters is associated with the fact that the measured conductivity, \( \sigma \), depends on both, the concentration, \( n \), of charge carriers and their mobility, \( \mu \), by \( \sigma = en\mu \), in which \( e \) is the elementary charge. In particular, in doped materials or composites such as the PEDOT:PSS, it is therefore difficult to distinguish whether an increase in conductivity is caused by an improved mobility of charge carriers or by an enhanced number of available mobile charge carriers.\(^\text{20} \) However, such information is essential to further improve the conductivity of well-processable PEDOT:PSS. One possible—albeit elaborate—approach to separate the two contributions consists in using time-domain terahertz transmission spectroscopy.\(^\text{21} \)

In our study, we use thermoelectric measurements to separate the contributions due to carrier concentration and carrier mobility. In contrast to the electrical conductivity, the Seebeck coefficient depends only on the carrier density, \( n \), yet not on their mobility, \( \mu \). One can therefore derive the effective macroscopic mobility of the charge carriers by comparing measurements of the Seebeck coefficient with those of the electrical conductivity. We have investigated the change in conductivity that results on modifying the PEDOT:PSS ratio from 1:1 to 1:30. Despite the large variation of the dopant PSS, we find the carrier concentration to be constant. The observed increase in conductivity by over three orders of magnitude can be quantitatively described using a percolation model based on a generalized effective media theory (GEMT).

**EXPERIMENTAL**

**Synthesis of the PEDOT:PSS Solutions**

The PEDOT:PSS samples with different PSS content were prepared using the Baytron P synthesis route.\(^\text{3} \) In this process, the monomer 3,4-ethylenedioxythiophene (purity 97%) is polymerized at room temperature in an aqueous solution of poly(4-styrenesulfonic acid) (average molecular weight \( M_w = 70,000 \)) in the presence of sodium persulfate (\( \text{Na}_2\text{S}_2\text{O}_8 \), purity 99%) as the oxidizing agent.

We presume that the monomer EDOT is fully converted to PEDOT in the presence of the poly(4-styrenesulfonic acid), the oxidizing agent, and the initiator.\(^\text{22} \) Therefore, the PEDOT:PSS solutions with different PEDOT-to-PSS-ratios were prepared by volumetric ratios of the aqueous solutions of EDOT and PSS with respect to the different densities of the educts as follows.

Ratios of EDOT-to-PSS between 1:1 and 1:30 were mixed in deionized water for 10 min to obtain aqueous solutions with 2.3 wt % of the EDOT:PSS mixture at room temperature. Subsequently, \( \text{Na}_2\text{S}_2\text{O}_8 \) was added at a ratio of 1 mol \( \text{Na}_2\text{S}_2\text{O}_8 \) to 2 mol 3,4-ethylenedioxythiophene and the solution was again stirred for another 10 min. After the addition of \( \text{Fe}_2\text{(SO}_4)_3 \) as an initiator, the polymerization started and resulted in a dark-blue dispersed PEDOT:PSS that was again stirred for 24 h. Finally, the solution was filtrated in vacuum using a filter with a porosity of 4–7 \( \mu \)m.

**Measurement of the Conductivity by Impedance Spectroscopy**

To determine the electrical conductivity by impedance spectroscopy and dc measurements, the PEDOT:PSS solutions were drop-cast on a defined area, masked with adhesive tape on alumina substrates (purity 96%) with screen-printed parallel gold electrodes (5744L, Dupont) that had been fired at 1123 K for 10 min. All PEDOT:PSS samples were properly dried under a dry nitrogen atmosphere and the measurements were also performed under dry nitrogen ambiance. The Au electrodes had a distance of \( s = 1.2 \) mm that were connected with Au wires to the measurement device and either the dc resistance or the impedance spectra were determined by 2-wire measurements.

Impedance spectra were taken using an impedance analyzer (Novocontrol Alpha-Analyzer) with an amplitude of 50 mV rms in the frequency range from 0.1 mHz to 20 MHz. The prepared PEDOT:PSS transducers were connected to the analyzer using a guarded sample holder. For each measured sample, the complex impedances, \( Z \), were plotted in the complex plane (Nyquist-Plot, \(-\text{Im}(Z)\) vs. \( \text{Re}(Z) \)). An equivalent circuit was obtained and the parameters resistance, \( R \), and capacitance, \( C \), were fitted using the least squares method.

By knowing the geometry and the resistance, \( R \), of the device under test, one can derive the electrical conductivity. For the calculation of the electrical conductivity, \( \sigma \), the thickness of the PEDOT:PSS film, \( d \), has to be known (eq 1).

\[
\sigma = \frac{s}{R \cdot A} = \frac{s}{R \cdot b \cdot d}
\]

In eq 1, \( s \) is the distance between the electrodes, \( R \) is the measured resistance, and \( A = b \cdot d \) is the cross-sectional area with the length of the electrodes, \( b = 6 \) mm, and the film thickness \( d \).

To determine \( d \), the surface profile was recorded using a surface-profilometer (Mahr Perthenmeter S2) after a small cavity was scratched into the PEDOT:PSS surface. As the thickness of the dried PEDOT:PSS layer could not be presumed to be uniformly planar, the relative deviation of film-thickness was estimated to be 20%.

**Measurement of the Thermopower**

The setup for measuring the Seebeck coefficient is depicted in Figure 1. The films are drop-cast on an alumina substrate (Rubalit 710, purity 99.6%) of a thickness of 250 \( \mu \)m, a length of 50 mm, and a width of 6.35 mm. An additional modulation heater generates an alternating temperature gradient over the PEDOT:PSS films. The temperature difference between the thermocouples TC1 and TC2, \( \Delta T = T_{TC2} - T_{TC1} \), is determined via the Au and Pt thermocouple tracks and contact pads, whereas the thermovoltage of the film, \( V_{\text{meas}} \), is measured between the Pt contacts.

The screen-printed Pt and Au conductor tracks form the thermocouples TC1 and TC2. As the Seebeck coefficients of Pt and Au, \( \eta_{\text{Pt}} \) and \( \eta_{\text{Au}} \), respectively, are known, the Seebeck coefficient \( \eta \) of the PEDOT:PSS film versus Pt can be...
determined from $V_{\text{meas}}$. It has to be corrected by the known Seebeck coefficient of platinum, $\eta_{\text{Pt}}$. Details of the evaluation of $\eta$ can be found in Ref. 24.

$$\eta = \eta_{\text{Pt}} - \frac{V_{\text{meas}}}{\Delta T}$$

(2)

The PEDOT:PSS film itself is 4 mm long and 4 mm broad. It is clear that Pt and Au are not the most suitable materials for room temperature thermocouples due to their low thermopower difference. However, these transducers are available as standard devices in our laboratory, and therefore, we used them for convenience. As the thermovoltage, $V_{\text{meas}}$, is a difference between two electrical potentials, it is independent on the geometry of the films. Therefore, an exact definition of the geometry (especially an exact thickness) of the films is not necessary. The PEDOT:PSS solutions were just dip-coated on a masked area of the transducer and then dried for 24 h. The so-prepared transducer were connected to a sample-holder and placed into a tube in which a flow (600 mL/min) of dry nitrogen-gas was introduced.

A periodic voltage, $V_{\text{heater}} = V_0 \cos(2\pi f_{\text{mod,heater}} t)$, was applied to the modulation heater. It generated the temperature difference $\Delta T = T_{\text{TC2}} - T_{\text{TC1}}$ with the frequency $f_{\text{mod}}$:

$$\Delta T = \Delta T_0 \cos(2 \pi f_{\text{mod}} t)$$

(3)

As heater power and applied modulation heater voltage show a quadratic relation, the temperature difference is modulated with the double frequency as the modulation heater voltage, that is, $f_{\text{mod}} = 2 f_{\text{mod,heater}}$. In eq 3, $\Delta T_0$ is the amplitude of the temperature modulation, $f_{\text{mod}}$ is the frequency of the temperature modulation, and $t$ is the time. $V_{\text{meas}}/\Delta T$ is determined by a regression analysis of many measured data pairs of the two signals $\Delta T_j$ and $V_{\text{meas},j}$. They are plotted according to the following linear equation:

$$V_{\text{meas},j} = a \cdot \Delta T_j + b$$

(4)

The slope, $a$, represents the quotient $V_{\text{meas}}/\Delta T$ for eq 2. This method allows to eliminate interfering offset voltages. Further details of the data evaluation procedure and accuracies are given in Ref. 25. For our experiments, $f_{\text{mod}} = 12.5$ Hz was used.

As described in Ref. 26, the thermal noise plays a crucial role. Our experiments revealed that the conductivity of PEDOT:PSS solutions with a PSS fraction $> 6$ is too low for the determination of the thermopower. Hence, the Seebeck coefficient could only be measured for PEDOT:PSS samples with ratios of 1:1.6, 1:2, 1:3, 1:4, and 1:6.

RESULTS

The conductivity of films made with PEDOT:PSS in ratios from 1:1 to 1:30 was determined by impedance measurement in the range from 0.5 Hz to 20 MHz. The Nyquist diagram in Figure 2. shows the complex impedances $Z$, normalized to the corresponding film thickness and plotted in the complex plane for the PEDOT:PSS in ratios from 1:7 to 1:30. As the electrode distance is the same for all samples, the curves thus represent the geometry independent complex impedances of the PEDOT:PSS solutions, subject to the inaccuracy of the thickness measurement. For the well conducting samples with ratios from 1:1 to 1:6, the impedance plots result in dots in the complex plane and are therefore not shown in Figure 2. Their resulting values were additionally confirmed by measurements using a dc digital multimeter.

The impedances show a semicircle at high frequencies and an adumbrated “tail” at low frequencies. The semicircles can be attributed to an equivalent circuit with a resistor parallel to a capacitor. The diameter of the semicircle gives a measure for the resistance, $R$. Several features are noteworthy.
First, the diameter of the semicircle, and thus the film resistance, increases with PSS content and second, the "tail" at low frequencies becomes more pronounced with increased PSS content.

The "tail" appears especially pronounced in Figure 3, in which an impedance spectrum down to 1 mHz is displayed for the sample with the most significant "low-frequency tail," the 1:30 sample. The "low-frequency tail" is a straight line in the complex impedance plane, with a phase angle of 43°. For a phase angle of 45°, such a behavior can be described by a so-called Warburg impedance. Such constant phase elements are typical for electrolytes measured with blocking electrodes.

The resistances, $R$, derived from the data in Figure 2 are given in Table 1, along with measured approximate thickness of the drop-cast film. The capacitance, $C$, of the equivalent circuit was found to be $9.3 \pm 3.5 \text{ pF}$, independent on the PSS content. This value is mainly due to the capacitance of the wiring and the alumina substrate used.

The conductivity, $\sigma$, results from the resistance values, $R$, according to eq 1. The conductivity as a function of PSS content is shown in Figure 4 in a semilogarithmic representation. The conductivity falls by more than three orders of magnitude from 2.3 (\(\Omega \text{cm}\))$^{-1}$ for PEDOT:PSS (1:1) to about $1 \times 10^{-3}$ (\(\Omega \text{cm}\))$^{-1}$ for a PEDOT:PSS ratio of 1:7. This value remains constant for higher PSS contents. The high value of 2.3 (\(\Omega \text{cm}\))$^{-1}$ for PEDOT:PSS (1:1) agrees well with values reported in Ref. 9.

To assess whether this strong decrease in conductivity on increasing the PSS content results from a variation in the concentration or in the mobility of the charge carriers, we have determined the Seebeck coefficient, $\eta$, for the samples with PEDOT:PSS ratios of 1:6 and below (Fig. 5). The low conductivity associated with a higher PSS content precludes measurement of the Seebeck coefficient due to a poor signal-to-noise ratio.

### Table 1: Resistance Determined from Figure 2 as well as the Respective Measured Film Thickness, $d$

<table>
<thead>
<tr>
<th>Solution</th>
<th>$R$ (kΩ)</th>
<th>$d$ (µm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>PEDOT:PSS 1:7</td>
<td>166</td>
<td>12.9</td>
</tr>
<tr>
<td>PEDOT:PSS 1:8</td>
<td>189</td>
<td>6.5</td>
</tr>
<tr>
<td>PEDOT:PSS 1:9</td>
<td>188</td>
<td>5.9</td>
</tr>
<tr>
<td>PEDOT:PSS 1:15</td>
<td>248</td>
<td>5.9</td>
</tr>
<tr>
<td>PEDOT:PSS 1:20</td>
<td>298</td>
<td>6.5</td>
</tr>
<tr>
<td>PEDOT:PSS 1:25</td>
<td>106</td>
<td>2.0</td>
</tr>
<tr>
<td>PEDOT:PSS 1:30</td>
<td>311</td>
<td>2.5</td>
</tr>
</tbody>
</table>
We find the Seebeck coefficient to be positive, as expected for a p-type semiconductor. Independent on the PSS content, the coefficient has a value of about 14 ± 3 μV/K. This value is lower than those reported for polythiophenes (up to 130 μV/K) or polycarbazoles (up to 71 μV/K) and it is higher than those known for polypyrrole (5 μV/K). Similar values have been reported for PEDOT:PSS by Liu et al., Jiang et al., or Scholdt et al.

For a material with conduction by polarons, the Seebeck coefficient can be related to the density of charge carriers according to eq 5:

$$\eta = \frac{k_B}{q} \left[ \ln \frac{1-c}{c} + \frac{A S_k}{k_B} \right]$$  \hspace{1cm} (5)

with Boltzmann’s constant $k_B$, the electrical charge, $q$ (here $+e$), the entropy of the lattice relaxation $S_k$ and the parameter $c = p/N$, that denotes the density of occupied sites, with the charge carrier concentration $p$ and the number of available sites per unit volume $N$. By knowing the Seebeck-coefficient, one can therefore calculate the charge carrier concentration by eq 6:

$$p = \frac{N}{\exp \left( \frac{q \eta}{k_B} - \frac{A S_k}{k_B} \right) + 1}$$  \hspace{1cm} (6)

According to eq 6, a constant Seebeck coefficient implies a constant charge carrier density, and hence, due to

$$\sigma = e \ p \ \mu_p$$  \hspace{1cm} (7)

A constant conductivity should result if one assumes a constant defect electron mobility $\mu_p$.

**DISCUSSION AND MODEL**

The fact that the Seebeck coefficient is constant within the experimental uncertainty for PEDOT:PSS ratios from 1:1 to 1:6 implies that within this range, the concentration of charge carriers does not depend on the PSS content. The dramatic change of electrical conductivity of more than three orders of magnitude that is observed in this composition range must therefore reflect a corresponding change in effective charge carrier mobility. This may be accounted for by the morphological structure of PEDOT:PSS.

According to the literature, the PEDOT:PSS complex consists of PSS chains to which PEDOT oligomer attach tightly, forming a stacked arrangement with the counter-ions. This ensemble forms a tertiary structure with a core of tangled PEDOT:PSS chains embedded in shells of a loosely crosslinked excess PSS. With increasing PSS content, one can presume that the effective distance between the PEDOT:PSS cores decreases. To explain the behavior of the PEDOT:PSS films with the high PSS contents, we consider the PEDOT:PSS material as a two phase system consisting of a PSS-saturated PEDOT:PSS "grain" that is diluted by the electrolyte PSS. The composite forms a p-type semiconductor, as is confirmed by the positive sign of the Seebeck coefficient $\eta$.

We first consider the electrical conductivity for samples with high PSS content such as a PEDOT:PSS ratio of 1:30. The impedance spectrum in Figure 3 yields a constant phase angle of almost 45° toward low frequencies. Such a distinct so-called Warburg impedance at low frequencies is typical for the interface of an electrode and an electrolyte. It implies that at this composition, the conductivity is fully dominated by the electrolyte and limited by the carrier transport through PSS. This is confirmed by the fact that the conductivity value of the PEDOT:PSS 1:30 sample found from our impedimetric measurements agrees with the measured DC conductivity of PSS ($1.1 \times 10^{-2} \ \Omega\text{cm}^{-1}$).

When lowering the PSS content, this constant phase element decreases and it disappears fully for PEDOT:PSS ratios between and 1:6 and 1:1. The conductivity of the PEDOT:PSS samples (Fig. 4) remains largely constant and low on decreasing the PSS ratio. This persists until a critical ratio of 1:6 is reached, where the conductivity increases steeply to higher values. To understand the origin of this sudden increase in conductivity, it is essential to know whether the change in the PEDOT:PSS ratio in the range from 1:6 to 1:1 is associated with a change in charge carrier density or whether it reflects a change in mobility (see eq 7). The constant Seebeck coefficient in this range (Fig. 5) implies a constant charge carrier density. Thus, varying the PSS ratio does not alter the doping level of the composite but only changes the amount of excess PSS that separates PEDOT:PSS complexes with a constant dopant level.

Such a system is reminiscent to blends of conducting polyaniline with an insulating polystyrene–polybutadiene–polystyrene block copolymer. The conductivity of the blend, considered to consist of flat polyaniline spheroids within a SBS matrix, is controlled by percolation between the conductive polyaniline sites. It can be modeled successfully using a GEMT. This theory has been developed from percolation theory and the effective media theory (see e.g. review Ref. 39). It was introduced for predicting the overall...
In eq 8, \( \Phi \) stands for the volume fraction of the highly conductive phase, with \( \Phi_m \) being the (critical) percolation volume fraction for the highly conductive phase. \( \rho_m = \sigma_m^{-1} \) is the specific resistance of the resulting material composite and the model parameter \( w \) denotes the critical exponent. Typically, \( w \) is a parameter that has to be adjusted to the experimental data and includes the different aspect ratios and distributions of the single material phases.

We have applied eq 8 to model the conductivity of the PEDOT:PSS films. As we varied the PSS content, the volume fraction of the low-conductive phase \((1-\Phi)\) is used to fit the conductivity. The PSS-content is normalized to the maximum PSS content considered here (PSS = 20). We considered the volume fraction of the PEDOT:PSS solution to be identical to the weight percent, as the percentage of weight for the PEDOT:PSS solution is lower than 3% and the density of both PEDOT and PSS are in same range than pure water. Figure 6 shows the experimental (marks) and calculated conductivity (drawn curve) of PEDOT:PSS using the GEMT (eq 8). For the high- and low-conductive phases, we used the constant conductivities, \( \sigma_h \) and \( \sigma_l \), of 2.3 \((\Omega \text{cm})^{-1}\) and \( 1 \times 10^{-3} \ ((\Omega \text{cm})^{-1}\), respectively, as found by our conductivity measurements, keeping in mind, that commercial grade PEDOT:PSS solutions with high PSS-content have a varying electrical conductivity in the order of half a magnitude.

The critical percolation volume fraction for the low-conducting phase was considered to be \((1-\Phi_c) = 0.15\), corresponding to a PEDOT:PSS ratio of 1:6. With these input parameters and a fit parameter of \( w = 1.05\), good agreement was obtained with the experimentally found conductivities. Thus, the conductivity of the PEDOT:PSS film can be accounted for by considering percolation between highly conducting PEDOT:PSS complexes embedded in a poorly conducting PSS matrix. This result has two remarkable implications. First, the concept of percolation entails an inhomogeneous distribution of the conductive PEDOT:PSS complexes in the insulating PSS matrix. At the percolation threshold, given by a PEDOT:PSS ratio of 1:6, some conductive complexes must be adjacent to allow for the formation of a conduction path. Consequently, the PEDOT:PSS complex cannot be surrounded entirely by a PSS shell of homogeneous thickness. Rather, for a PSS content below 1:6, the PSS layer between two adjacent PEDOT:PSS complexes must disappear.

Second, the percolation model is based on the notion that the low-conductivity phase and the high-conductivity phase have an intrinsic, constant (and naturally different) conductivity. Correspondingly, this also implies a constant intrinsic mobility for each phase. The composition-dependent measured conductivity results from the number of percolation paths that are formed, and consequently, the composition-dependent macroscopic charge carrier mobility of the sample corresponds to an averaged, effective mobility. It is limited by the number of percolation paths formed and it is much lower than the intrinsic mobility of the neat PEDOT:PSS complex, that is, the highly conducting phase of the composite.

At this point, it is useful to keep in mind that measuring the thermovoltage means to measure a potential difference. It is only important, what the potential between two points of different defined temperatures is. Hence, it does not matter, whether one determines the voltage between two points of a homogenous film of the material, or of a porous system, or even of small paths. As long as the same material is involved, the thermovoltage (and therefore also the Seebeck coefficient) remains independent of geometry. Hence, if one expresses the conductivity, measured by eq 1, in terms of eq 7, the constant Seebeck coefficient, and the concomitantly constant carrier density imply that the charge carrier mobility changes with PSS content. From the applicability of the GEMT, it is now evident that only the effective, averaged mobility changes while the intrinsic mobility of the two phases remains unaffected.

We finally comment on the suitability of the PEDOT:PSS composite for thermoelectric applications such as energy conversion purposes. The performance of a thermoelectric material is often assessed using the thermoelectric power factor, PF, given by the product of conductivity and the square of the Seebeck coefficient, \( \text{PF} = \sigma \text{SE}^2 \). For the PEDOT:PSS system we investigated, the highest PF is therefore obtained for the 1:2 ratio to be \( 2.8 \times 10^{-8} \text{ W/K}^2\text{m} \). This value is one magnitude lower than reported earlier.\(^9\) Compared to other conducting polymers, the PF of our investigated PEDOT:PSS-System is in the same range than Polypyrrole and Polyaniline derivates \((\sim 10^{-8} \text{ W/K}^2\text{m})\).\(^{44}\)

In addition to the PF, the figure-of-merit, ZT, is used to estimate the efficiency of thermoelectric materials in
thermoelectric devices. It is defined by $ZT = (PT)^2/\kappa$, with the thermal conductivity $\kappa$. The highest $ZT$ of the PEDOT:PSS system almost $5 \times 10^{-5}$ for the 1:2 ratio at 298 K when assuming $\kappa = 0.17$ W/mK.

In other words, we describe PEDOT:PSS as a system of an electronic p-type conductor (PEDOT) that is diluted in PSS, an ionic conductor. As long as there are percolation paths, one measures the Seebeck coefficient of the electronic conductor. When the percolation threshold is reached, that is, when no percolation paths exist anymore, the PEDOT:PSS behaves fully ionic.

In addition, we demonstrate that measurements of the Seebeck coefficient can be used to differentiate between changes in the charge carrier density and changes in the mobility. Our results show that the Seebeck coefficient, and thus the doping level in the PEDOT:PSS system is independent of PSS content in the measured range. Concomitantly, we determined the thermoelectric properties of PEDOT:PSS and measured a Seebeck of $14 \pm 3 \mu V/K$, which is consistent with earlier investigations.

**REFERENCES AND NOTES**