Thermopower and high-pressure electrical conductivity measurements of template synthesized polypyrrole

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We present results of high-pressure–low-temperature studies of template synthesized polypyrrole. Thermopower measurements at ambient pressure show a linear temperature dependence, which supports the intrinsic metallic character of the samples. The dc conductivity follows the typical variable-range-hopping behavior at low temperatures. The application of pressure results in an increasing localization length and an enhancement of the conductivity, especially at very low temperatures. The comparison with bulk samples of polypyrrole suggests that the template synthesis increases the localization length of the charge carriers, which in turn results in an increase of the dc electrical conductivity. [S0163-1829(96)06947-0]

I. INTRODUCTION

Polypyrrole (PPY) is one of the conducting polymers which is superior to, e.g., polyacetylene because of its chemical and physical stability and its insensitivity with respect to oxygen in the doped form. Martin and co-workers[1–4] recently developed an interesting approach for preparing conductive polymer nanostructures called template synthesis. This name reflects the fact that the polymer is synthesized and doped within the pores of commercial nanoporous host membranes. The product of this synthesis is an ensemble of almost equally sized polymeric microtubules embedded in the host membrane. The dimensions of these microtubules depend on the pore diameter and membrane thickness. Various diameters between 10 and 1000 nm have been synthesized.[1] After synthesis the microtubules were freed by dissolving the polycarbonate host membrane. The microtubules can be deposited and compacted on the surface of various substrates to form thin films. The conductive microtubules show a higher degree of molecular and supermolecular order than is present in the same polymer synthesized by conventional methods.[2,3] It has been suggested that the polymer chains are highly aligned,[2] which explains the higher electrical conductivity of the template-synthesized forms. The temperature of synthesis is a further crucial point for the optimization of the electrical properties. As shown by Cai *et al.*,[2] the conductivity can be further enhanced by decreasing the synthesis temperature.

In the present paper we report the results of low-temperature electrical measurements on thin films composed of template synthesized polypyrrole microtubules with two different diameters, and compare these results with data obtained from bulk polypyrrole. High pressure is applied in order to investigate possible pressure-induced changes of the electrical conduction process, and to obtain a deeper insight into the physical mechanisms of the conduction process.

II. EXPERIMENT

Polypyrrole was synthesized within the pores of Nuclepore polycarbonate membranes using conventional oxidative polymerization at $0\,°C$.[1–3] Two pore diameters, 400 nm (sample PPY 400) and 50 nm (PPY 50), were chosen. The 400- and 50-nm-diameter microtubules had wall thicknesses of about 60 and 20 nm, respectively. We used paratoluene-sulphonate (PTS) as the dopant, and achieved doping levels of about 30%. After synthesis, the microtubules were freed from the template membrane, collected on filter paper, and compacted to yield tubule-based thin films. The microtubules are randomly oriented within the films. The film thickness was determined from secondary-emission-monitor images of the edges of a cut sample as about 3 μm for PPY50 and 6 μm for PPY400. Electrochemically prepared bulk material doped with PTS was been synthesized as a reference material. The high-pressure, low-temperature electrical properties of this sample are described in Ref. 5.

The polypyrrole samples are prepared for the electrical measurements by cutting small strips of size 7×3 mm,[2] and evaporating four Au contacts onto the film surface. The gold contacts are connected to 25-μm platinum wires using silver paint. Four-probe conductivity measurements are performed with an ac (16 Hz) resistance bridge (Linear Research Corp.). In order to avoid sample heating as well as the possible influence of nonlinearities due to electrical field effects, the excitation voltage was reduced to less than 2 mV.
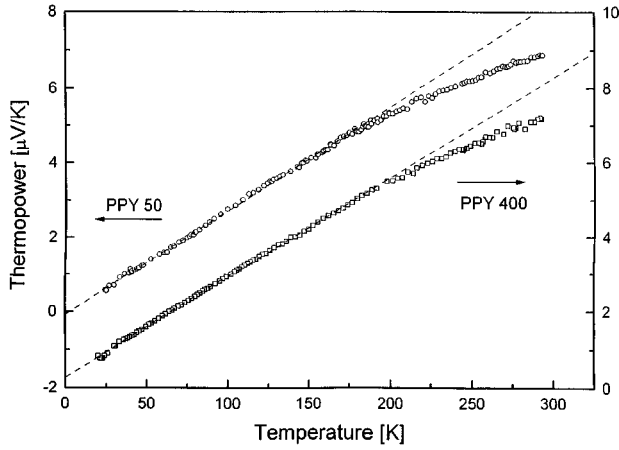
The thermopower was measured using a steady-state

FIG. 1. Temperature dependence of the thermopower of samples composed of 400- (PPY 400) and 50-nm (PPY 50) template synthesized polypyrrole microtubules.

FIG. 2. Temperature dependence of the resistance of bulk polypyrrole (Δ) and samples composed of 50- ($\bigcirc$) and 400-nm- ($\square$) diameter polypyrrole microtubules.

method. Two well-calibrated Cu-chromel thermocouples were employed to monitor both the thermovoltage and reversible temperature difference of 0.5–1 K. Small metal film heaters were attached to each side of the sample, and alternately a current was switched on and off to input a uniform heat pulse through the sample. In all cases, all data were corrected for the contribution of the Cu leads, which can be determined separately using a standard Pb sample.

For high-pressure investigations the samples are put in a Teflon container together with a K-type thermocouple and a lead manometer for temperature and pressure measurements, respectively. Fluorinert, FC-77, is used as the pressure transmitting liquid. This container is placed in a beryllium copper high pressure clamp cell[6] designed for a maximum pressure of 2 GPa. The clamp cell itself fits into a He cryostat allowing measurements down to 1.2 K. The temperature below 40 K is determined by a Ge resistor.

III. RESULTS AND DISCUSSION

A. Thermopower and electrical conductivity at ambient pressure

Since, to our knowledge, the thermopower of template synthesized polypyrrole has not been published before, we would like to include it here to demonstrate that our samples behave in the same way as it is expected from highly conducting bulk samples. The thermopower of both PPY samples is shown in Fig. 1 from room temperature to about 20 K. The thermopower is a linear function of T below 200 K. Such a linear behavior of the thermopower has been observed before in electrochemically synthesized polypyrrole films,[7] and has been attributed to the highly conducting clusters. Analogously we suggest that the experimental linear contribution to the thermopower found in our samples reflects the high conductivity of the microtubules.

Both samples, composed of 50- and 400-nm microtubules, respectively, show an almost identical temperature dependence of the thermopower. Since the thermopower is an intrinsic property of the polymer chain, it follows that the microscopic chain structure is similar for both microtubulus diameters.
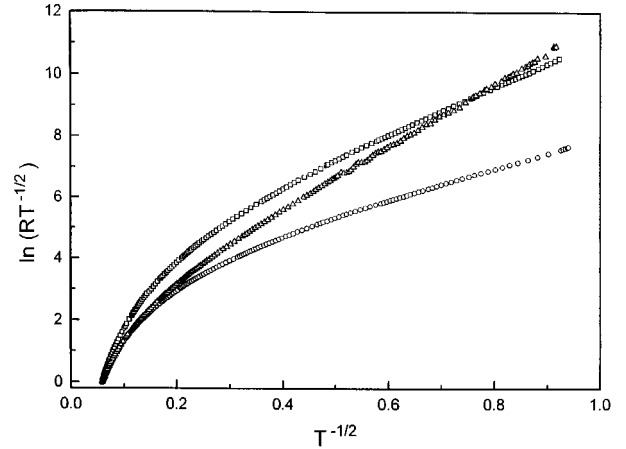
The electrical conductivity has room temperature values of 30 and 50 S cm^{-1} for PPY50 and PPY400, respectively. These values seem to be in contradiction with the observation that the room-temperature conductivity of template synthesized polypyrrole increases with decreasing diameter of the microtubules.[2] However, the compressed films still exhibit a high degree of porosity due to the high stability of the polypyrrole microtubules.[1] Since the porosity also changes with the diameter of the microtubules, the calculated values do not reflect the intrinsic conductivity of the material, and may provide an explanation for the observed reversal.

In order to obtain information about the intrinsic conductivity and the microscopic conduction process the temperature dependence of the resistance has to be considered. It is plotted for both samples composed of template synthesized microtubules and for bulk polypyrrole in Fig. 2. The resistance instead of the conductivity has been displayed due to the fact that we do not know the pressure and temperature dependence of the sample dimension. At low temperatures ($T < 4$ K) the resistance follows the Mott variable-range-hopping model[8] with exponent $\frac{1}{2}$, as indicated by the linear behavior in that region. It is worthwhile to mention here the controversy concerning the direct application of the Mott model to one-dimensional variable range hopping.[9,10]

In order to obtain more insight into the nature of the conduction process at low as well as at high temperatures, we apply the method proposed by Hill.[11] If we assume a resistivity of the general form

$$R = A T^{-b} \exp\{(T_0 T)^p\}, \qquad (1)$$

where b, T_0, and p are considered to be unknown but determinable parameters, the activation energy

$$\Delta E = \frac{d(\ln R)}{d(1/kT)}$$

is given by

$$\Delta E = b k T + T_0^p p k T^{1-p}. \qquad (2)$$

The exponent p is a characteristic quantity describing the physical mechanism for hopping conduction. In the high-

temperature limit, nearest-neighbor hopping with $p=1$ is expected to be the dominant conduction process. With decreasing temperature the nearest-neighbor hopping changes to the variable range hopping characterized by an exponent $p=\frac{1}{4}$ for a three-dimensional hopping process.[8] At very low temperature the Coulomb interactions of the localized charge carriers have to be taken into account. It has been shown[12–14] that there is a Coulomb gap in the density of states due to this interaction, which results in a change of the exponent $p=\frac{1}{4}$ to $p=\frac{1}{2}$. However, the exponent $p=\frac{1}{2}$ may also arise from a one-dimensional variable-range-hopping process without a Coulomb gap in the density of states.

The determination of p from the experimental data is reliable, if the temperature dependence of the resistance is mainly determined by the exponential term in Eq. (1). This is guaranteed for strongly localized charge carriers, where the weak temperature dependence of the prefactor T^{-b} can be neglected. Highly conducting polymers, however, show a more complicated temperature dependence of the resistance. The charge carriers are weakly localized resulting in a small value for T_0 in Eq. (1). Therefore, the prefactor in Eq. (1) cannot be neglected in the moderate- to high-temperature region. Only at very low temperatures is the exponential dependence in Eq. (1) expected to become the leading term.

The template synthesized polypyrrole samples in this study are highly conducting polymers. Hill's plot of $\ln(\Delta E)$ versus $\ln(T)$ in Figs. 3(a) and 3(b) shows different slopes in the high- and low-temperature limits. At high temperatures $\ln(\Delta E)$ is a linear function of $\ln(T)$ with a value of the slope equal to 1. Equation (2), with the exponent $p=1$, provides an explanation for this behavior. It shows that the dominating hopping process is nearest-neighbor hopping, and that the prefactor T^{-b} determines the temperature dependence of the resistance. The value of $b\approx0.7$ is in the range of exponents derived from various theories.[15] The domination of the temperature dependence by the prefactor in Eq. (1) also explains that the Arrhenius plot of $\ln(R)$ versus $1/T$ does not show the linear dependence in the high-temperature range, as might be expected for the nearest-neighbor hopping process.

At very low temperatures ($T<4$ K) the slope of the Hill's curve in Figs. 3(a) and 3(b) changes to a value of $\frac{1}{2}$, indicating that variable range hopping is the dominating conduction mechanism. In this case the resistance is given by

$$R\propto T^{1/2}\exp\{(T_0/T)^n\}, \quad n=1/(1+D), \quad (3)$$

where D is the dimension of the conduction process,[8] and is plotted in Fig. 2. As can be seen, the data are fitted well with the exponent $\frac{1}{2}$. The prefactor $T^{1/2}$ is due to multiphonon processes,[8] and is important in the variable-range-hopping region. It is not connected with the prefactor T^{-b}, which determines the high-temperature behavior of the resistance.

If the exponent $\frac{1}{2}$ is due to a preferentially one-dimensional hopping path or to the formation of a Coulomb gap in the density of states cannot be decided from the present experiment. The very low-temperature range where the exponent $p=\frac{1}{2}$ is observed may favor the influence of Coulomb interactions.

A comparison of the conductivity data of the template synthesized polypyrrole samples with bulk polypyrrole with the same dopant[5] reveals that the template samples have a weaker temperature dependence. The different temperature
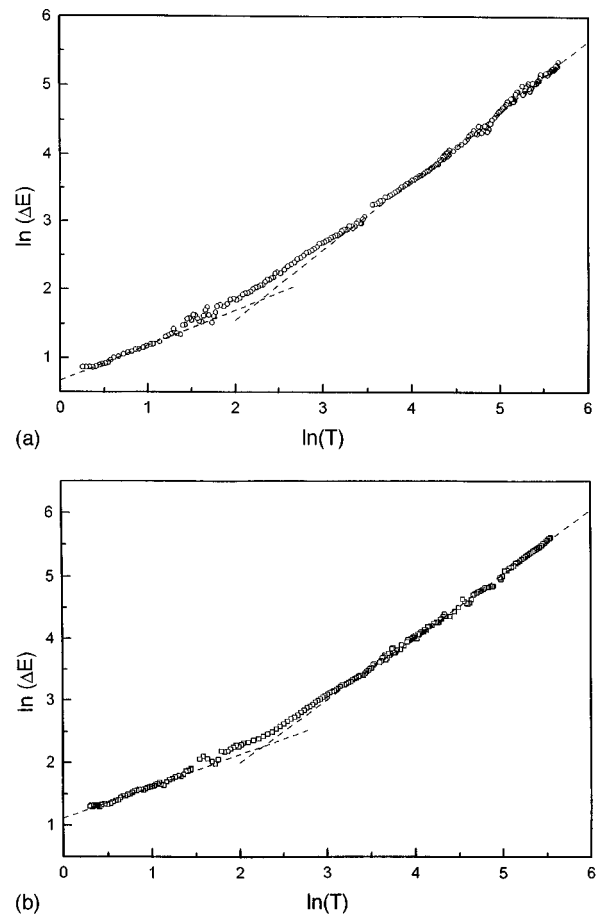

FIG. 3. (a) Hill's plot of a sample composed of 50-nm-diameter microtubules. (b) Hill's plot of a sample composed of 400-nm-diameter microtubules.

dependence of the template and bulk sample resistance are shown in Fig. 2. The most significant differences are observed at low temperatures. As a quantitative measure, we compare the ratios $R(295$ K$)/R(4.2$ K$)$ and $R(295$ K$)/R(1.2$ K$)$, and the slopes of the curves at low temperatures expressed by the Mott temperature T_0, in Table I. Especially at very low temperatures the template samples are better conducting than the bulk polypyrrole. The resistance decreases with decreasing diameter of the microtubules, as has also been observed in room-temperature measurements.[2] Furthermore, the increase of the resistance with decreasing temperature is considerably smaller for the sample composed of small-diameter microtubules, as has been demonstrated reproducibly with many samples as long as care was taken to

TABLE I. Comparison of the electrical properties of template synthesized and bulk polypyrrole. The columns show the Mott temperature T_0 in the variable-range-hopping region and ratio of the resistance values at room and low temperatures.

Sample	T_0/K	$R(295$ K$)/R(4.2$ K$)$	$R(295$ K$)/R(1.2$ K$)$
bulk polypyrrole	107	80	3368
template PPY 400	58	79	694
template PPY 50	26	23	122

protect them from moisture. This is quantitatively expressed by the Mott temperature T_0 in Table I.

According to the Mott variable-range-hopping theory, the Mott parameter T_0 is inversely proportional to the localization length of the charge carriers. Therefore, strong localization (small localization length) results in a high value of T_0 and a large resistance increase at low temperatures. Weakly localized charge carriers are characterized by a small value of T_0, and the variable-range-hopping region is shifted to very low temperatures. From the decrease of T_0 with decreasing microtubule diameter, we conclude that the template synthesis results in an increased localization length of the charge carriers. This can be due to an increased intramolecular and intermolecular order, to a decreased number of defects and disturbances of the polymer structure, to an extension of the conjugation length, or to a combination of these effects.

B. Conductivity at high pressure

The application of hydrostatic pressure results in an increase of the room-temperature conductivity. The ratio of high pressure (2 GPa) and ambient pressure conductivities is obtained as 1.3 and 1.8 for PPY 50 and PPY 400, respectively. The value of 1.8 compares well with the pressure coefficient of 1.7 for bulk polypyrrole.[5] The small-diameter microtubules, however, show a distinctly weaker pressure dependence of the conductivity at room temperature. The same tendency is observed in the temperature dependence of the resistance at different constant pressures [Figs. 4(a) and 4(b)]. At low temperatures the pressure effect on the resistance is even larger than the one observed at room temperature, since the slope of $\ln(R*T^{-1/2})$ versus $T^{-1/2}$ decreases with increasing pressure. However, the pressure dependence of the resistance at all temperatures is weaker for the small-diameter microtubules. The weaker pressure dependence of the sample composed of the small-diameter microtubules is displayed even more clearly in Fig. 5, where we plotted the pressure dependence of T_0 in the variable-range-hopping region for bulk polypyrrole and samples composed of 400- and 50-nm-diameter microtubules. For all samples, $T_0(P)$ can be described by an exponential decay. The values of T_0 decrease by factors of 12.5, 5.8, and 4.7 for bulk polypyrrole, PPY 400, and PPY 50, respectively, if the pressure increases to 2 GPa.

It should be noted that extrapolations of the low-temperature Mott curves with slope T_0 to infinite temperature (i.e., to $T^{-1/2}=0$) in Figs. 4(a) and 4(b) tend to a value which is independent of pressure. The main pressure effect consists in the reduction of T_0, whereas the prefactor in Eq. (1) does not change with pressure.

IV. CONCLUSION

The enhancement of the conductivity of samples composed of template synthesized microtubules is pronounced at low temperatures due to a weaker temperature dependence and a decreased Mott temperature in the variable-range-hopping region. The application of pressure results in a further increase of conductivity with respect to the ambient pressure value. The change of the low-temperature conduc-
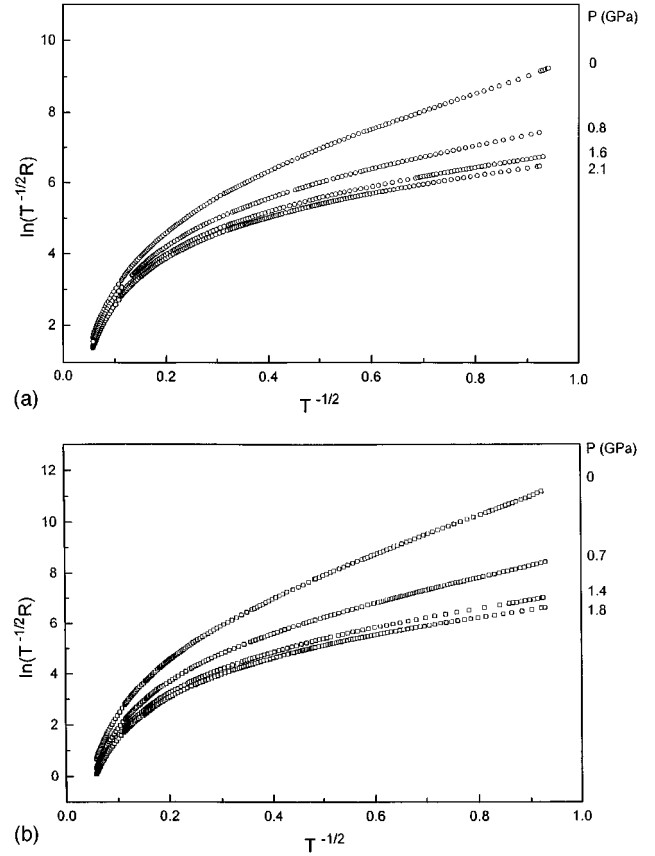

FIG. 4. (a) Temperature dependence of the resistance of a sample composed of 50-nm-diameter polypyrrole microtubules at different pressures. (b) Temperature dependence of the resistance of a sample composed of 400-nm-diameter polypyrrole microtubules at different pressures.
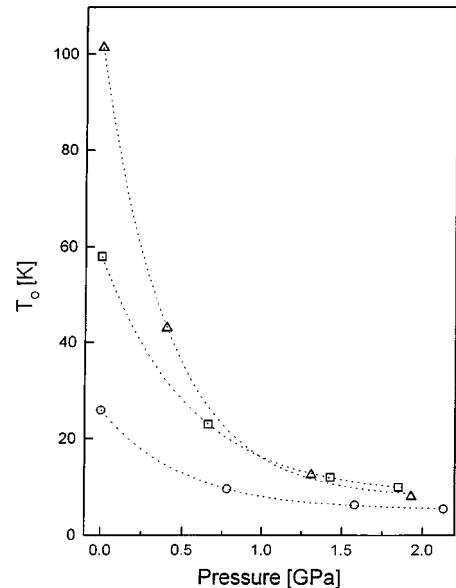

FIG. 5. Pressure dependence of the Mott temperature T_0 of bulk polypyrrole ($\triangle$) and of samples composed of 50- ($\bigcirc$) and 400-nm- ($\square$) diameter polypyrrole microtubules

tivity can be explained by a pressure-induced decrease of the characteristic Mott temperature T_0. According to the variable-range-hopping model, T_0 is a function of the localization length 1, and the density of states at the Fermi level, $N(E_F)$

$$T_0 = 1^{-D} N(E_F)^{-1}, \tag{4}$$

where D is the dimension of the conduction process.

Assuming that $N(E_F)$ shows only a small pressure dependence, we can conclude that the localization length can be increased by the choice of the method of synthesis as well as by the application of hydrostatic pressure. In the case of template synthesis it is expected that there is an increased orientational molecular ordering and a suppression of defects caused by the interaction of the polymer with the pore wall during synthesis. The application of pressure results in a higher overlap of the electronic wave functions, in the reduction of topological defects, and in an increase of the conjugation length. It is interesting to note that the highly conduct-

ing sample composed of 50-nm-diameter microtubules shows the smallest pressure effect. The largest pressure dependence of the conductivity is observed in the bulk polypyrrole samples. This general tendency suggests that the template synthesis produces a well-ordered state, which is obtained for the bulk polypyrrole only by the application of high pressure. At the highest pressure in this experiment the low-temperature properties of all samples are similar, as can be seen from the values of the Mott temperatures at 2 GPa in Fig. 5. Therefore, the positive influence of pressure on the electrical properties of conducting polymers can be achieved at ambient pressure by using the template synthesis.

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