

Thermal Properties of Conducting Polypyrrole Nanotubes

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Thermal properties of polypyrrole nanotubes synthesized by the chemical oxidation of pyrrole with iron(III) chloride in the presence of methyl orange as structure-guiding template, have been investigated. As-prepared polypyrrole salt and corresponding base were compressed into pellets. Thermogravimetric analysis has shown that the heating/cooling of both polymers is connected with water desorption/re-absorption. This process influences all temperature dependences of the thermophysical properties. The specific heat of both polypyrrole forms was the same at 35 °C. The thermal diffusivity of polypyrrole base was lower than that of the salt. The dilatational characteristics are strongly influenced by water desorption/re-absorption. Water desorption is connected with the contraction of polypyrrole and its re-absorption with the expansion of polypyrrole. The electrical resistivity was measured, in analogy to thermal experiments, by a four-point van der Pauw method. The electrical resistivity was 0.016 and 10.2 Ωcm at room temperature, for both materials. The electrical resistivity was also influenced by water desorption/re-absorption as well as other thermophysical properties.

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1. Introduction

Polypyrrole (PPy), one of the most studied conducting polymers, is widely used in various applications, including corrosion protection, sensors, secondary battery electrodes, supercapacitors, etc. [1–4]. PPy can be easily prepared by chemical oxidation [5] or electrochemical polymerization of pyrrole monomer [6]. According to the method of synthesis, it can be prepared in the form of thin films or powders. PPy is commonly used as a conducting filler [7] as well as a matrix for conducting composites [8].

Properties of the materials based on polypyrrole are sensitive to the conditions of preparation. There are many important parameters determining the properties of PPy such as temperature of polymerization [9], the type of oxidant and its molar concentration, to name just few. The polypyrrole salt is a polycation [5]. The nature of its counter-ions can greatly influence morphology as well as the electrical conductivity of the resultant polymer. For example, Carrillo et al. [10] studied the influence of dopant anions on the properties of PPy-coated poly(styrene-*co*-methacrylic acid) particles. They found that aromatic sulfonate anions increase the stability of the conducting polymer provided they are the only dopant. On the contrary, the presence of chloride as counterion had a detrimental effect not only on electrical

conductivity but also on the stability of the polymer. A similar conclusion has recently been reported for polyaniline a related in terms of hydrogen bonding [11]. An effort has been invested in the study of various morphologies of PPy such as nanotubes or nanofibers since it is expected that especially electrical properties would be improved [12].

This was indeed the case, since PPy nanotubes were found to have a conductivity of 40–70 S cm⁻¹ [13], considerably higher than that the ordinary globular form. Such nanotubes are obtained when the oxidation of pyrrole has been carried out in the presence of methyl orange, as reported in many recent papers [13–16].

While electrical properties are of prime interest, thermal properties of PPy [14] have not been virtually reported in the literature despite their vital importance particularly in the design of composites. The difference in the thermal properties of the components, such as thermal expansion, can determine lifetime of those materials. The thermal stability and thermal conductivity become of importance in fuel cells and other devices operating at elevated temperature.

The thermal stability assessed by the thermogravimetric analysis (TGA) on neat PPy has shown that the initial weight loss below 100 °C is due to the volatilization of humidity and as well as residual monomers [17]. In another study [18], the TGA of PPy doped by dodecylbenzene-sulfonic acid has shown the first weight loss at 110 °C due to the release of water. The second weight loss started at about 244 °C and it was connected with the evaporation or degradation of acid or both.

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PPy is predominantly used in the form of films or various mixtures. In these materials two or more components are in direct contact. The thermal properties of single components are then responsible for utility properties of these composite materials especially during their thermal treatment. Any polymer material that is exposed to ambient atmosphere and temperature can be assumed as thermally treated. The thermal conductivity as well as thermal expansion are two properties determining various thermal and residual stresses between two composite components. The thermal conductivity has been studied for PPy by Saxena et al. [19].

The coefficient of thermal expansion (CTE) is a parameter which determines the character of interfacial interactions when PPy is used as a component of composite materials. Dilatometry measures all strains in the material because all these strains are additive. No systematic research dealing with the thermal expansion of PPy has yet been made. Large differences between published CTE values are presented in literature. One can find a large negative CTE reported by Lin [20] on the electrochemically deposited PPy film on carbon. A large shrinkage of PPy during heating reduced thermal expansion of carbon coated with a PPy film in comparison with uncoated one. In another communication [21], the CTE for the PPy nanowires was found to be positive, $1.2 \times 10^{-5} \text{ K}^{-1}$.

The changes of thermal and mechanical properties of polymers start usually at low temperatures, near or slightly above the room temperature. Plastic flow and relaxation phenomena in polymers are both strongly temperature dependent at elevated temperatures. Already fluctuations of ambient temperature thus influence physical and chemical properties of the polymers. It is known that polymers are generally viscoelastic materials where all physical properties are dependent on time. When water or further components are released during heating the mass of material changes during measurement. It is evident that the classical approach for research and use of the thermophysical properties cannot be applied for these materials in the same manner as for example for elastic materials. The aim of this work is the determination of the thermophysical properties as a function of time and mass changes during the thermal cycle. Thermogravimetric analysis was therefore the first and basic method used before determination and analysis of the temperature dependences of thermophysical properties. The thermal properties such as the thermal diffusivity, the specific heat, the thermal expansion as well as the electrical resistivity are studied for PPy nanotubes. An influence of salt-to-base conversion in PPy on thermal properties is also investigated and analyzed.

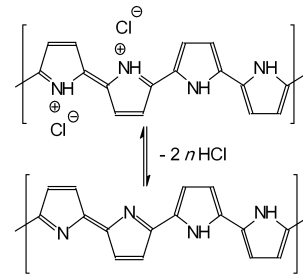
2. Experimental

2.1. Preparation

Polypyrrole nanotubes were prepared by chemical oxidation of pyrrole monomer with iron(III) chloride hexahydrate in the presence of methyl orange [13]. 1 mL of pyrrole was added to 287 mL of 2.5 mM methyl orange

solution in distilled water. Then, 33 mL of 434 mM iron(III) chloride hexahydrate solution in distilled water was added dropwise over two hours into the reaction solution. Reaction solution was kept at 5°C and stirred for 24 h. The molar concentration of reactants thus were 45 mM pyrrole, 45 mM iron(III) chloride hexahydrate, and 2.2 mM methyl orange. The PPy nanotubes were collected by filtration, purified by Soxhlet extraction using acetone until the extract was colorless. Then PPy nanotubes were rinsed with ethanol and dried at 40°C in vacuum.

PPy was studied in the protonated form, as a PPy salt, and as deprotonated form, PPy base (Scheme 1).



Scheme 1.

Polypyrrole salt (hydrochloride) converts in alkaline media into a corresponding base. The deprotonation of PPy salt to PPy base was made by the suspension of PPy salt in excess of 1 M ammonium hydroxide [22]. The deprotonation process results in the decrease of chloride counterions content in the polymer structure. Polymer powders were compressed in pellets with a manual hydraulic press with the load of 7 tons. PPy nanotubes (Fig. 1) display the one-dimensional structure that it favourable for electrical conduction in the composite materials.

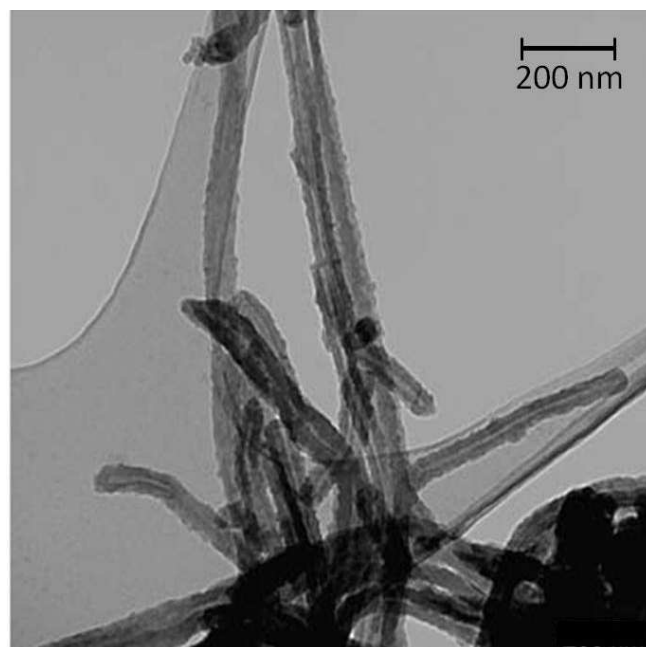


Fig. 1. Microstructure of polypyrrole nanotubes (TEM).

2.2. Thermal characterization

Basic thermal characteristics were obtained by TGA and differential scanning calorimetry (DSC) method (SETARAM). The specific heat was determined by the latter method. Experiments were made in static helium atmosphere as well as in dynamic atmosphere with heating/cooling rates 2 and 10 K min⁻¹.

The thermal diffusivity was measured by using a flash method [23] in air. The front side of the flat pellet was irradiated by a short energy pulse from a Xe-pulse flash lamp. The time dependence of the temperature rise was determined on the opposite side of the sample by an infrared detector (Kolmar Technologies), diffusivity a could be calculated from the formula $a = 0.1388L^2/t_{0.5}$, where L is the sample thickness and $t_{0.5}$ is the so-called half-time, i.e. the time at which a half of the maximum temperature rise is reached. The thickness of the pellets was 1.2–1.5 mm.

The linear thermal expansion of the samples was measured in air using a Netzsch 402 C/4/G dilatometer. The maximum temperature during the thermal cycle was 70 °C. Various temperature profiles were used during measurements of dilation characteristics. The accuracy of the apparatus was checked by determining the coefficient of thermal expansion of magnesium and comparing it with the data available in the literature. The agreement between the measured values and the values reported in the literature is in the range $\pm 3\%$.

2.3. Resistivity

The samples for resistivity measurements were prepared as pellets with a diameter of 13 mm and a thickness of about 1 mm. Each measurement was done with a four-point method in van der Pauw arrangement of contacts. The T behavior of resistivity was studied in two regimes: (1) a sample localized in chamber with ambient atmosphere (not pumped space) and (2) a sample under dynamic vacuum, when the chamber is continuously evacuated by a rotary pump, down to a pressure lower than 10 Pa. During measurement in the first regime, the samples were placed in a Janis Research VPF-475 cryostat, used as an oven chamber in the range 32–60 °C. The T inside the cryostat was controlled using a LakeShore 330 Autotuning Temperature Controller. Temperature of the sample was monitored with a thermocouple. For resistivity measurements, a Keithley 6220 Precision Current Source, a Keithley 2182A Nanovoltmeter and a Keithley 7002 Switch System equipped with a Keithley 7011-S Quad 1×10 Multiplexer Cards were used. For experiment in dynamic vacuum, the samples were placed in a Janis Research VNF-100 cryostat. The temperature of the samples was controlled by a LakeShore 332 Temperature Controller and was kept constant at about 32 °C during pumping. Resistivity was measured using a Keithley 237 High-Voltage Source Measurement Unit and a Keithley 2010 Multimeter equipped with a 2000-SCAN 10 Channel Scanner Card.

3. Results and discussion

3.1. TGA and DSC

TGA was studied between the room T and 70 °C (Fig. 2). The mass loss was revealed for PPy salt as well as for PPy base. Two heating rates 2 and 10 K min⁻¹ were used for both polymers. Only in case of PPy salt heated at 10 K min⁻¹ rate, the mass of the sample stayed practically constant. The highest mass loss was found for PPy base heated with a rate of 2 K min⁻¹. The lower heating rate the higher weight loss was found. It is assumed that the weight loss is due to the water desorption. The specific heat of the PPy salt and PPy base was determined by DSC method using the heating rate of 10 K min⁻¹. This method assumes that mass of sample is constant during the whole measurement. This requirement is fulfilled only for the case of PPy salt at the heating rate of 10 K min⁻¹.

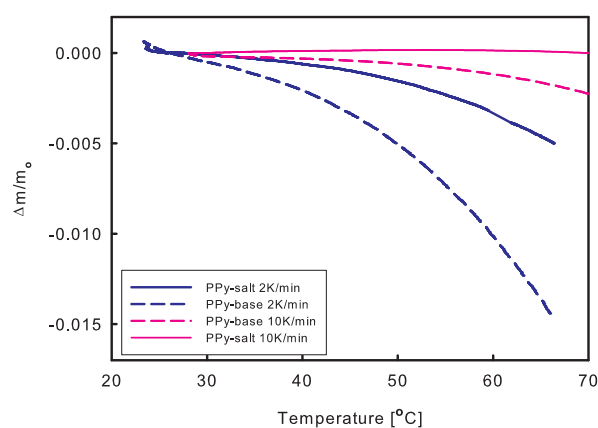


Fig. 2. Temperature dependence of the relative change of the sample mass $\Delta m/m_0$ for PPy salt and PPy base (heating rate is indicated for each type of material).

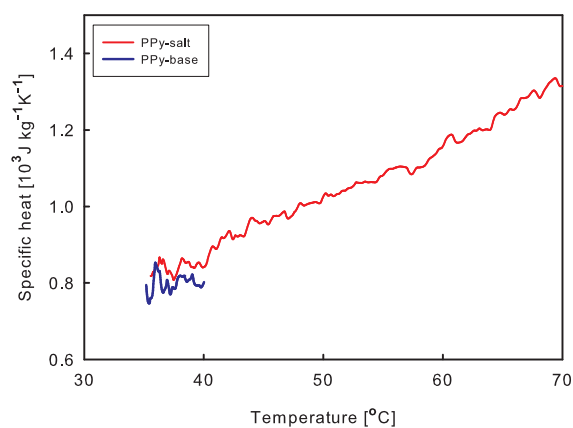


Fig. 3. Temperature dependence of the specific heat for two materials.

The temperature dependence of the specific heat is displayed in Fig. 3. The specific heat of the PPy base is presented in the figure only at about the room T because only at these temperatures the weight of the sample can

be assumed to be constant. The specific heat of the PPy salt increased linearly with increase of temperature in the whole studied temperature range. These results are in good agreement with the specific heat values found on PPy films by Lunn et al. [24], where values of 800–1400 J kg⁻¹ K⁻¹ were found in the temperature range 7–67 °C.

3.2. Thermal diffusivity and thermal conductivity

The thermal diffusivity results for both PPy forms (Fig. 4) show that the thermal diffusivity is practically independent of the sample thickness. The thermal conductivity is determined as product of the thermal diffusivity, the density, and the specific heat (see the Table). The thermal conductivity values are lower than the results presented by Lunn et al. [24] where thermal conductivity obtained on films was 0.86 W m⁻¹ K⁻¹. The thermal conductivity of various types of samples can be different.

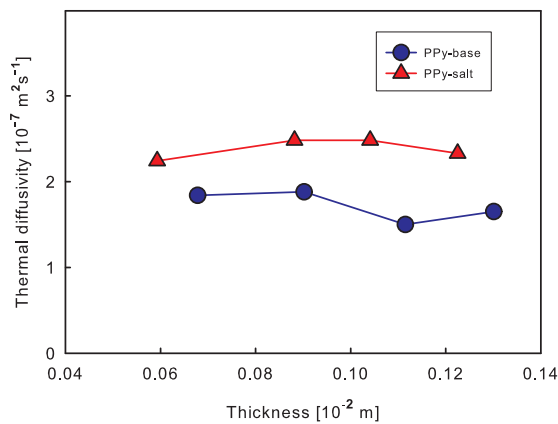


Fig. 4. Thickness dependence of the thermal diffusivity for PPy salt and PPy base.

TABLE

Thermal properties of PPy salt and PPy base at the room temperature.

PPy	Density [$\frac{\text{g}}{\text{cm}^3}$]	Specific heat [$\frac{\text{J}}{\text{kg K}}$]	Thermal		Electrical resist. [Ωcm]
			diff. [$\frac{\text{m}^2}{10^7\text{s}}$]	cond. [$\frac{\text{W}}{\text{m K}}$]	
Salt	1.32	800	2.3	0.24	0.016
Base	1.40	800	1.8	0.20	10.2

3.3. Thermal expansion

Thermal expansion characteristics have been determined for PPy salt as well as for PPy base (Fig. 5). The temperature dependence of the relative elongation and CTE are shown for the second runs. Both temperature dependences were followed by the isothermal range where the sample temperature was held at 25 °C for 10 h. Thermal expansion characteristics for both forms of PPy polymers differ. In the whole studied T range, the PPy base has a lower CTE ($20 \times 10^{-6} \text{ K}^{-1}$ at 30 °C) than the PPy salt ($35 \times 10^{-6} \text{ K}^{-1}$ at 30 °C). While the CTE of

PPy salt increases with increase of T , the CTE of PPy base decreases. This decrease is a consequence of massive release of water (Fig. 2).

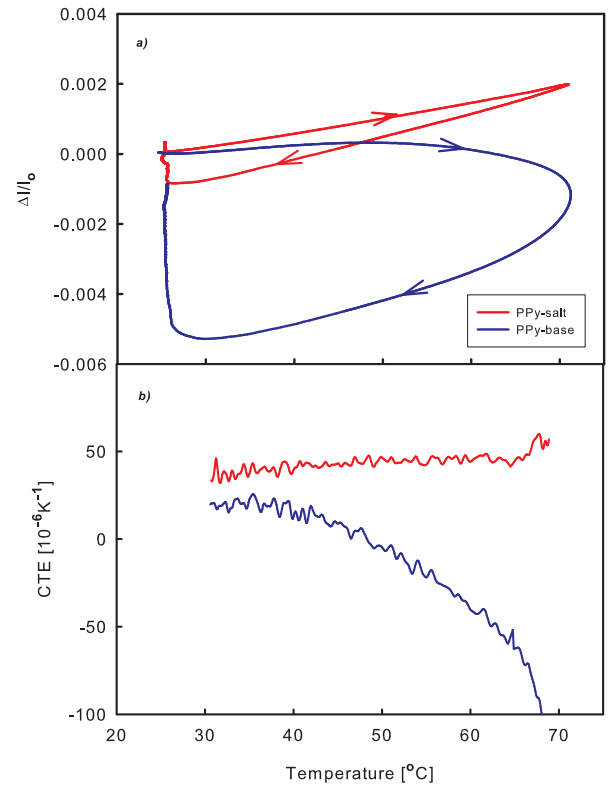


Fig. 5. Temperature dependence of (a) the relative elongation $\Delta l/l_0$ and (b) the coefficient of thermal expansion (CTE).

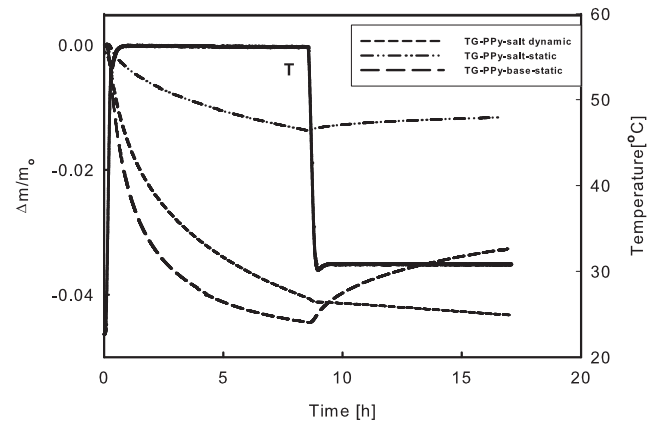


Fig. 6. Time dependence of the temperature and the relative sample mass $\Delta m/m_0$.

PPy is known to be a humidity-sensitive conducting polymer [25]. In this work sorption-induced strain of the PPy films measured at 25 °C increased with the amounts of absorbed water. It is evident that, for the interpretation of our dilatational results, the knowledge of the polymer behavior with respect to water quantity contained in polymer during the heating/cooling cycle is necessary.

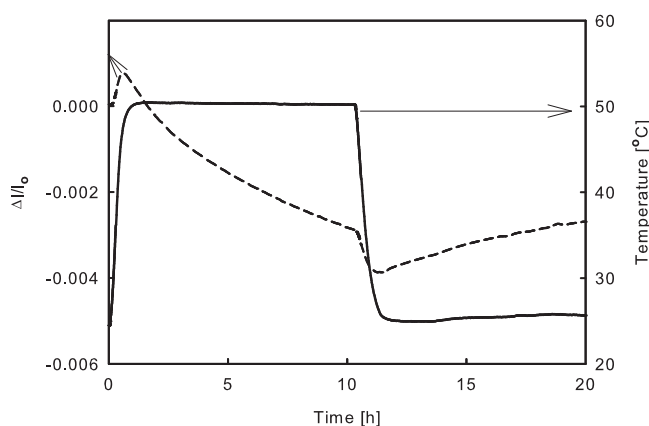


Fig. 7. Time dependence of the temperature and the relative elongation $\Delta l/l_0$.

To obtain this information, the dilatational and TGA experiments have been made for PPy salt with the same temperature profiles (Fig. 6). The sample was heated at 2 K min^{-1} rate to 55°C , and held there for 8 h. The decrease of the temperature at the rate 2 K min^{-1} to 30°C was followed by isothermal range at this temperature for 8 h both in a static as well as a dynamic (20 ml min^{-1}) atmosphere. The mass loss takes place from the lowest temperatures during heating as well as along the isothermal segments. This mass loss is a consequence of water desorption. If the experiment is made under dynamic conditions, the desorbed water is removed from the measured volume. The isothermal part of the experiment at room temperature takes place in an atmosphere without water in the gas phase. Water cannot be re-absorbed and the mass of sample slowly decreases. In static experiments, desorbed water stays in the device space and it is again absorbed after cooling. All processes are time dependent. Figure 6 shows also the TGA results for PPy base in static regime. In all three cases, the main mass loss is bound to the isothermal range, where the mass of samples decreases with increase of time. Changes of the sample mass are small during dynamic temperature changes in all cases.

The highest mass loss was observed for PPy base in static regime. This decrease is 4 times higher as compared with PPy salt in static regime. In the last isothermal segment, the mass of sample slowly increased in both cases. This is a consequence of re-absorption of water from the device space. Water desorbed from the sample during isothermal high temperature step stays bound on cold parts of the device and its diffusion to the sample is evidently the slowest step of this process. Comparison of the TGA results for PPy salt in dynamic and static arrangements shows that the release of water from the sample strongly depends on the presence of water in the gas phase.

It was mentioned that absorption/desorption of water is connected with the sample strain [26]. Dilatational experiments made in the static air atmosphere confirm

these findings. Dilatation results presented in Fig. 7 (only PPy salt was measured) were made with the same temperature profile as TGA (Fig. 6). When we compare isothermal segments in Figs. 6 and 7, we can see that there is the same tendency in both methods. Desorption of water leads to contraction of the sample and its expansion is a consequence of the water re-absorption.

Dilatometry measures all strains that take place in the material during thermal treatment. All strains are additive. We can see that at least, two kinds of strains exist in PPy salt during heat treatment:

The first strain is due to thermal vibrations of particles. Thermal expansion generally occurs if there are anharmonic interactions between vibrating particles. The vibrational amplitudes of a mode as a function of temperature determine the expansion behavior. The amplitudes are expressed by the density of phonons which are excited at a given temperature. Various vibrational modes can be activated in polymers due to their chain structure. Interchain stretching vibrations are always positive. Transverse vibrations exhibit a different behavior. With increase of temperature the amplitudes of transverse vibrations get larger and the chain length gets smaller. This results in a negative component to the thermal expansion in the chain direction. A complication in the theoretical study of the thermal expansion of polymers is the entanglement of chains. An important factor for thermal expansion is the large free volume between chains.

The strain due to thermal vibration of particles is predominant in dynamic segments (Fig. 7, relative elongation increases/decreases). Rate of heating/cooling in these segments was 2 K min^{-1} . Water starts to release even at this heating rate (Fig. 2). The relative elongation even in these segments is the sum of two strains, a positive (in isotropic polymers positive interchain vibrations dominate over negative transverse vibrations) due to thermal vibration and a negative one due to release of water.

The second type of strain is due to absorption (desorption) of water. During all isothermal experiments where the temperature is above room temperature, the relative elongation decreases with increase of time. Thermogravimetric experiments with the same isothermal segments always show sample mass loss. We can assume that desorption of water leads to shrinking of the sample (the present samples do not exhibit anisotropy in dilatation characteristics).

3.4. Electrical resistivity

Since the electrical resistivity is the property of main interest in conducting polymers, it is crucial to know how it is influenced by various thermal treatment or water adsorption/desorption cycles.

Electrical resistivity measurements were conducted for highly conducting polypyrrole salt (from the resistivity point of view more interesting than PPy base form) in analogy to the dilatometric and TGA experiments at constant heating rate of 2 K min^{-1} from 32 up to 60°C and

followed by 10 h isothermal scanning at 60 and 32 °C, respectively (Fig. 8). During heating, the relative resistivity (RR) decreases up to 60 °C. Further decrease in RR takes place along the isothermal range when the sample is maintained at 60 °C. In 10 h, RR decreased at about 60% of the value of decrease approached during heating to final temperature, 60 °C. Subsequent increase in RR is connected with the temperature decrease from 60 °C to 32 °C. During the last stage, isothermal measurement at 32 °C, the RR further increased by 20% from the value of increase approached during cooling to 32 °C. Significant non-isothermal changes are in agreement with an expected semiconducting behavior. This is due to thermally activated behavior of charge carriers while any other effects on resistance, such as mass loss and elongation/contraction, are probably negligible. However, the changes of RR during isothermal measurement, the long-term decrease at 60 °C, and subsequent increase at 32 °C could be correlated with results of TGA (Fig. 6), the water release and its readsorption in PPy in the static ambient atmosphere, respectively. The discrepancy or only partial recovery is probably due to different sorption characteristics at various temperatures but some irreversible changes could not be excluded.

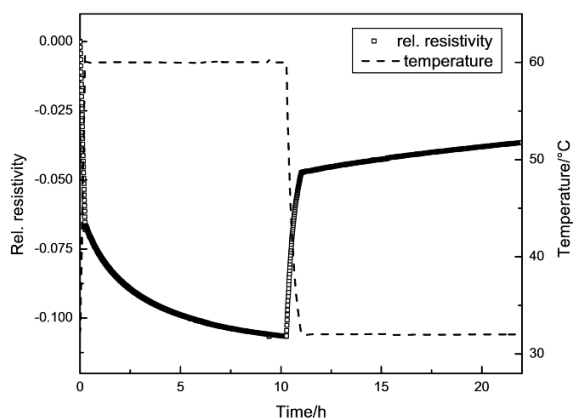


Fig. 8. Time dependence of the temperature (dashed line) and the relative change of resistivity (squares).

The effect of moisture on resistivity has already been studied in conducting polymers, mainly polyaniline [26–28], but it is still not completely understood despite its crucial importance. Isothermal resistivity at 32 °C in static atmosphere (Fig. 9) is compared to measurement in the dynamic vacuum (< 10 Pa). The former is the last stage of experiment described above. The resistivity increased, which is believed to be related to water adsorption. In the latter experiment, on the contrary, temperature was held constant at 32 °C from the beginning. Subsequent dynamic vacuum causes water removal from the sample. The resistivity decreased in the similar way than it increased in the former experiment. This supports our hypothesis of the role of water in electrical transport, particularly as the limiting agent. Increase in resistance of PPy due to the presence of water in atmo-

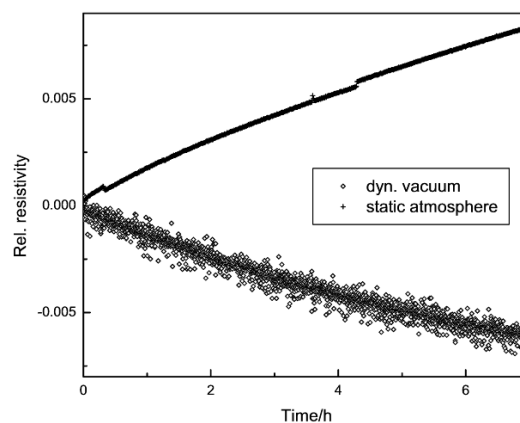


Fig. 9. Time dependence of the relative change of resistivity at 32 °C in static atmosphere (after heating to 60 °C, crosses) and in dynamic vacuum (circles).

sphere was reported in electropolymerized PPy tetrafluoroborate [29]. On the other hand, an initial promotion of conductivity of water-treated PPy granular films has been observed but enhanced ageing then followed [30]. The deeper study of water effect on conducting polymers is thus still needed.

4. Conclusions

Thermal properties of PPy nanotubes have been studied in the temperature range from the room temperature up to 70 °C. TGA has shown a substantial mass loss when the temperature increased. This mass loss is due to desorption of water that is a time-dependent process. TGA shows that after decreasing temperature down to the room temperature, water re-absorbed, if there was atmospheric humidity. The process desorption/re-absorption of water during of heating/cooling thermal cycle influences the character of the temperature dependences of the thermal expansion and the electrical resistivity. Desorption of water leads to the contraction of PPy samples and to decrease in the electrical resistivity. Re-absorption of water leads to expansion PPy and to increase of the electrical resistivity. The higher the T , the higher the mass loss, the higher contraction of PPy, and the more pronounced decrease of its electrical resistivity was found. PPy base exhibits higher mass loss than PPy salt. This is associated with higher a contraction of PPy base and a lower CTE for this type of PPy. The specific heat of PPy salt and PPy base are practically the same at the room temperature. The thermal diffusivity and the thermal conductivity of PPy salt are higher than of PPy base.

Acknowledgments

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