FTIR reflectance studies of electrochemically prepared polypyrrole films

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Abstract. Optical properties of polypyrrole (PPY) films electrochemically prepared in different conditions were investigated by FTIR reflectance spectroscopy in the range $200–6000\,\mathrm{cm^{-1}}$. The effects of some relevant electrochemical parameters (the electrolyte, the polymerization current density, and the deposition time) on the reflectance spectra of polypyrrole are reported. The optical constants for polypyrrole films were calculated from the reflectance spectra by Kramers–Kronig technique. The decrease of the electropolymerization current density and film thickness results in an increase of the reflectance and dc conductivity values for PPY(TSO).

Among conducting polymers polypyrrole (PPY) presents additional features such as good mechanical properties and environmental stability. dc conductivities in the range $10–100\,\mathrm{S/cm}$ are usually obtained for the electrochemically prepared polypyrrole films. Recently the metallic behaviour of highly conducting ($\sigma = 350\,\mathrm{S/cm}$) polypyrrole doped with hexafluorophosphate [PPY(PF$_6$)] was reported [1–4]. Comparative studies of polypyrrole films doped with PF$_6^-$ and with toluene sulfonate (TSO$^-$) ions were done by Kohlman et al. [2, 4]. For both types of polypyrrole films the reflectance indicates a metallic behaviour, increasing with decreasing frequency in the infrared, but different behaviours were observed for the real part of the dielectric function (ε_1). In the case of PPY(PF$_6$), ε_1 is negative for frequencies less than a screened plasma frequency ($\omega_{\mathrm{p}} = 250\,\mathrm{cm^{-1}}$), attributed to the free carriers. In contrast, for PPY(TSO), ε_1 is positive for all optical frequencies due to the localization of the carriers. The greater crystallinity ($\approx 50\%$) for PPY(PF$_6$), prepared at low temperature, accounts for the improved metallic behaviour of these films. PPY(TSO) films doped to the same level ($\approx 33\%$) as PPY(PF$_6$) are more disordered, $\approx 25\%$ crystalline [4]. However, the good environmental stability of polypyrrole films doped with organic ions such as TSO$^-$ [5]

makes them interesting for applications. The improvement in the polymer structural characteristic requires a deeper understanding of the correlation between the synthesis conditions and the polymer properties.

In this paper we present the correlation between the optical properties and the electrosynthesis conditions of polypyrrole films. Different electrolyte concentrations and current densities were used for the electropolymerization of polypyrrole. Specular reflectance measurements were performed on free-standing polypyrrole films by FTIR spectroscopy in the range $200–6000\,\mathrm{cm^{-1}}$. The optical constants for polypyrrole films were calculated from the reflectance spectra by Kramers–Kronig technique. The behaviour of the dc conductivity in the temperature range $130–423\,\mathrm{K}$ is presented. Our data shows that the polymerization current density and the film thickness have significant effects on the optical properties of polypyrrole.

1 Experimental

1.1 Sample preparation

The electrochemical synthesis of polypyrrole was carried out with different electrolyte types (p-toluene sulfonic acid, HTSO; lithium perchlorate, LiClO$_4$; and tetrabutyl-ammonium-tetrafluoroborat, Bu$_4$NBF$_4$). The electrolyte concentration, c_{e}, was varied in the range $0.01–0.15\,\mathrm{M}$. The polymerization was carried out in galvanostatic conditions at room temperature using different current densities: $0.25 \le j \le 1.25\,\mathrm{mA/cm^2}$. Polypyrrole films with thicknesses h in the range $10–25\,\mu\mathrm{m}$ were obtained. The film thickness was measured by using an electronic micrometer having an accuracy of $0.015\,\mathrm{mm}$. The area of the investigated films was $1\,\mathrm{cm^2}$. Two days was the elapsed time from the film preparation until measurements of properties for all the samples. The samples were washed in acetonitrile and dried under vacuum at room temperature just before the electrical and optical measurements.

1.2 Electrical measurements

The dc conductivity of the free-standing polypyrrole films was determined by the four-point-contacts method. The electrical contacts were made by silver paste. The measurements of dc conductivity temperature dependence in the range 130–423 K were performed in a cold-finger cryostat under vacuum. The temperature was measured with a diode type 1N4148 having 2 mV/K sensitivity in the investigated temperature range.

1.3 Optical measurements

Specular reflectance measurements in the range 200–6000 cm^{-1} were performed by FTIR spectroscopy on a Bomem MB-102 spectrophotometer. The absolute value of sample reflectivity was determined relative to the reflectivity of an aluminium mirror.

The optical constants for polypyrrole films were calculated from the reflectance spectra by Kramers–Kronig (K–K) technique. Since K–K transformation requires the knowledge of the reflectance at all frequencies, extrapolations of the experimental data were made beyond the measurement range. For wavenumbers $\nu < 200$ cm^{-1} the reflectance was extrapolated using the Hagen–Rubens relation [6]. At higher wavenumbers ($\nu > 6000$ cm^{-1}) the data were extrapolated by a decay function as ν^{-s} with $1 \le s \le 4$.

2 Results and discussion

2.1 dc conductivity

Room-temperature conductivities, σ_{dc} of free-standing polypyrrole films electrochemically prepared at different electrolyte concentrations and different current densities are given in Table 1. The higher dc conductivities were obtained for PPY(TSO) electrochemically prepared at lower electrolyte concentration (c_e=0.01 M) and lower current densities ($j \le 0.625$ mA/cm^2).

The temperature dependence of σ_{dc} for the investigated polypyrrole samples follows Mott's relation [7] for three-

Table 1. Room-temperature conductivities of polypyrrole samples electrochemically prepared in different conditions

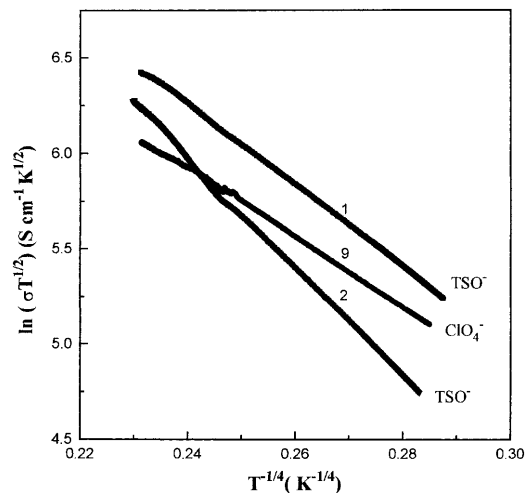| Sample	Doping ion	c_e / M/l	j / mA/cm^2	h / μm	σ_{dc} / S/cm
1	TSO$^-$	0.01	0.625	18	20
2	TSO$^-$	0.05	0.625	25	13
3	TSO$^-$	0.1	0.625	15	29
4	TSO$^-$	0.15	0.625	20	10
5	TSO$^-$	0.01	0.625	10	77
6	TSO$^-$	0.01	0.25	10	85
7	TSO$^-$	0.01	1.25	10	30
8	ClO$_4^-$	0.01	0.625	15	24
9	ClO$_4^-$	0.05	0.625	20	29
10	BF$_4^-$	0.01	0.625	20	32
11	BF$_4^-$	0.1	0.625	20	39

Fig. 1. Mott plots of dc conductivity for polypyrrole films electropolymerized at constant current density, $j = 0.625$ mA/cm^2 with different electrolyte concentration: 1, PPY(TSO), $c_e = 0.01$ M/l; 2, PPY(TSO), $c_e = 0.05$ M/l; 9, PPY(ClO$_4^-$), $c_e = 0.05$ M/l. The fitting parameters from Mott's equation (1) are: 1, $T_0 = 2.5 \times 10^5$ K, $\sigma_0 = 6.5 \times 10^4$ S cm^{-1} K$^{1/2}$; 2, $T_0 = 8 \times 10^5$ K, $\sigma_0 = 4.7 \times 10^5$ S cm^{-1} K$^{1/2}$; 9, $T_0 = 1.2 \times 10^5$ K, $\sigma_0 = 3.5 \times 10^4$ S cm^{-1} K$^{1/2}$

dimensional variable-range hopping (VRH):

$$\sigma(T) = \sigma_0 T^{-\frac{1}{2}} \exp\left[-(T_0/T)^{\frac{1}{4}}\right] , \qquad (1)$$

$$T_0 = \frac{16\alpha^3}{k_B N(E_F)} , \qquad (2)$$

$$\sigma_0 = 0.39 \left[N(E_F)/\alpha k_B\right]^{\frac{1}{2}} \nu_0 e^2 , \qquad (3)$$

where α^{-1} is the decay length of the localised state, ν_0 a hopping attempt frequency, $N(E_F)$ the density of states at the Fermi energy level.

In Fig. 1 the plots of $\ln(\sigma T^{1/2})$ as a function of $T^{-1/4}$ for several polypyrrole samples are given. The fitting parameters σ_0 and T_0 are in agreement with the reported results in the literature [8,9]. Variable range hopping is the dominant charge transport mechanism in our polypyrrole samples.

2.2 Reflectance spectra

The reflectance spectra of PPY(TSO) films (samples 1–4 from Table 1), electrochemically prepared with different electrolyte concentrations at a constant current density, $j = 0.625$ mA/cm^2 are shown in Fig. 2. For samples 1–3, prepared in the concentration range 0.01–0.1 M the reflectance increases with the increasing of the electrolyte concentration. The diffuse scattering contribution of the sample surface morphology to the reflectance does not allow a correlation between the reflectance and dc conductivity values for polypyrrole films thicker than 10 μm. We consider that the surface morphology of TSO$^-$-doped polypyrrole films depends strongly on the thickness of the electrochemically prepared sample. The surface roughness decreases with the decrease of the sample thickness. The inset in Fig. 2 shows the reflectance spectra for PPY(TSO) films with different thicknesses (samples 1 and 5 from Table 1), prepared in the same electrochemical conditions ($j = 0.625$ mA/cm^2, $c_e = 0.01$ M).
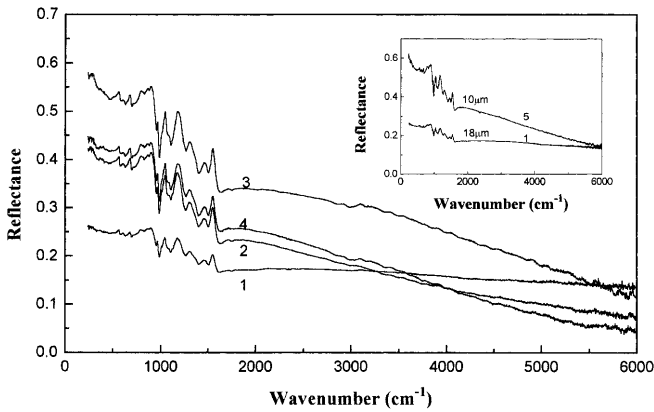
Fig. 2. Reflectance spectra of PPY(TSO) films electropolymerized at constant current density, $j = 0.625$ mA/cm^2 with different electrolyte concentration: 1, $c_e = 0.01$ M/l; 2, $c_e = 0.05$ M/l; 3, $c_e = 0.1$ M/l; 4, $c_e = 0.15$ M/l. The inset shows reflectance spectra of PPY(TSO) films with different thicknesses electropolymerized in the same conditions

Fig. 4. Reflectance spectra of polypyrrole films electropolymerized with different doping ions in the same conditions: $j = 0.625$ mA/cm^2, $c_e = 0.01$ M/l. 5, PPY(TSO), $\sigma_{dc} = 77$ S/cm; 8, PPY(ClO$_4^-$), $\sigma_{dc} = 24$ S/cm; 10, PPY(BF$_4^-$), $\sigma_{dc} = 32$ S/cm

In Fig. 3 we can compare the reflectance spectra for PPY(TSO) films, 10 μm thick, electrochemically prepared at the same electrolyte concentration, $c_e = 0.01$ M with different current densities (samples 5–7 from Table 1). Significantly higher reflectance was obtained for PPY(TSO) samples 5 and 6, electrochemically prepared at lower current densities. We have to point out the correlation between the reflectance and σ_{dc} values for these 10-μm-thick PPY(TSO) samples, i.e. the reflectance increases with increasing σ_{dc}.

The increase of the reflectance at lower frequencies indicates a metal-like behaviour. The reflectance increases more slowly in this region for PPY(TSO) sample 7 electrochemically prepared at high current density (Fig. 3) as well as for PPY(TSO) samples with thicknesses higher than 10 μm (Fig. 2). This behaviour can be explained by the structural differences between the samples electrochemically prepared in different conditions [10]. The increase of the electropolymerization current density and of the deposition time (for thick films) results in a greater structural disorder of TSO$^-$-doped polypyrrole. Besides, the change of the surface morphology can be influenced by the film thickness growth.

Figure 4 shows the reflectance spectra for PPY(TSO), PPY(ClO$_4$), and PPY(BF$_4$) electropolymerized in the same conditions: $j = 0.625$ mA/cm^2, $c_e = 0.01$ M (see Table 1).
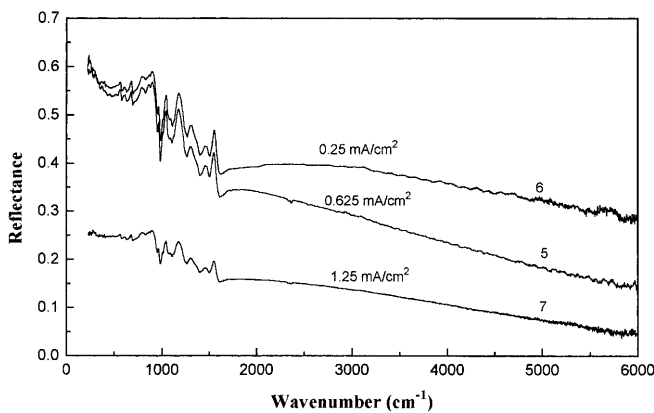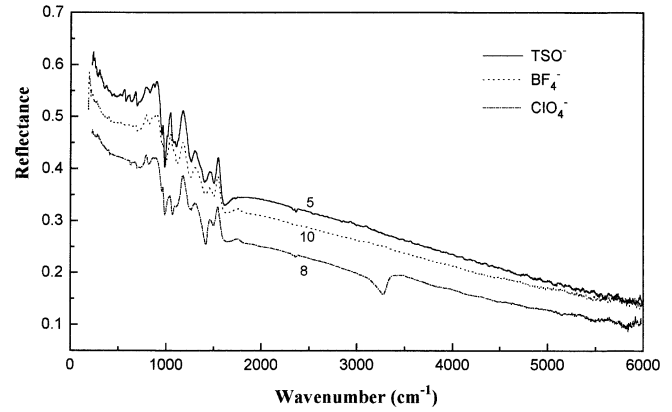

Fig. 3. Reflectance spectra of 10-μm-thick PPY(TSO) films prepared at $c_e = 0.01$ M/l with different electropolymerization current densities

From Fig. 4 one can see that the film thickness is not a relevant parameter for the reflectance of PPY(ClO$_4$) and PPY(BF$_4$). Although the samples have different thicknesses, the reflectance and dc conductivities values are correlated.

The real and imaginary parts of the refractive index, $n(\omega)$ and $k(\omega)$ were calculated from the reflectance spectra by the Kramers–Kronig technique [11, 12]. n is the absolute refractive index and k is the extinction coefficient. The real and imaginary parts of the dielectric function were calculated from n and k values, using the relations [11]:

$$\mathrm{Re}(\varepsilon) = \varepsilon_1 = n^2 - k^2 , \tag{4}$$

$$\mathrm{Im}(\varepsilon) = \varepsilon_2 = 2nk = \frac{\sigma_{op}}{\omega \varepsilon_0} . \tag{5}$$

Spectral dependencies of ε_1 and ε_2 for PPY(TSO), sample 5 are shown in Figs. 5 and 6, respectively. The real part of the dielectric function, $\varepsilon_1(\omega)$ is positive in all the spectral range. All the investigated polypyrrole samples from Table 1 show similar spectral dependencies for the real and imaginary parts of the dielectric function. This behaviour indicates that most charge carriers are localized in our polypyrrole samples [4, 6].

The optical conductivity, σ_{op} for polypyrrole samples was calculated from (5). In Figs. 7 and 8 the optical conductivities for polypyrrole samples are given. The low-frequencies behaviour of optical conductivity indicates that the free-carriers band has a weak contribution. The values of σ_{op} extrapolated at $\omega = 0$ are higher than that for σ_{dc}. This difference is higher for the samples with lower dc conductivity.

The effective number of carriers contributing to the optical properties over a finite frequency range was calculated from:

$$N_{eff}(\omega) = \frac{2m^*V}{\pi e^2} \int_0^\omega \sigma(\omega') \, d\omega' , \tag{6}$$

where $N_{eff}(\omega)$ is the effective number of carriers per unit cell contributing to the conductivity at frequencies below ω, V is the volume of the unit cell, and m^* is the effective mass of the electron. The volume V of the unit cell was calculated with the dimensions $a = 11$ Å, $b = 4.4$ Å, and $c = 3.5$ Å,
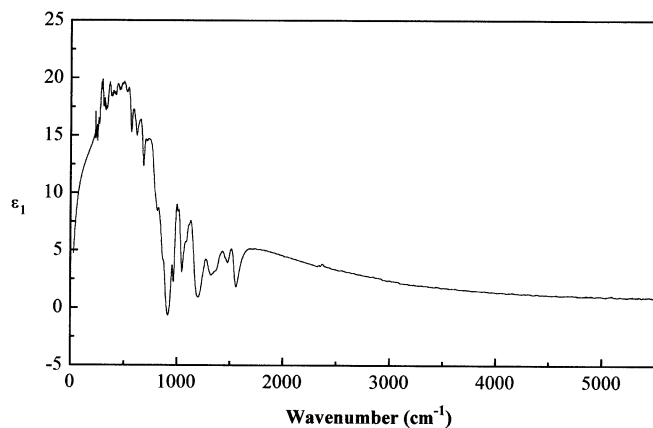
Fig. 5. The real part, ε_1, of the dielectric function for PPY(TSO) sample 5
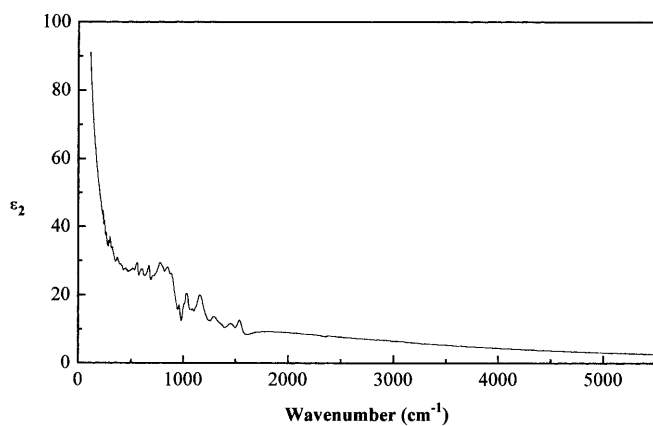
Fig. 6. The imaginary part, ε_2, of the dielectric function for PPY(TSO) sample 5

Fig. 7. Optical conductivities for PPY(TSO) samples: 1, $\sigma_{dc} = 20$ S/cm; 2, $\sigma_{dc} = 13$ S/cm; 3, $\sigma_{dc} = 29$ S/cm; 4, $\sigma_{dc} = 10$ S/cm. The inset shows the spectral distribution of the effective number of carriers per unit cell, N_{eff}

Fig. 8. Optical conductivities for polypyrrole samples electropolymerized with different doping ions: 5, PPY(TSO), $\sigma_{dc} = 77$ S/cm; 8, PPY(ClO$_4^-$), $\sigma_{dc} = 24$ S/cm; 10, PPY(BF$_4^-$), $\sigma_{dc} = 32$ S/cm. The inset show the spectral distribution for N_{eff}

taken from the X-ray diffraction analysis [10]. The values that we found for the parameters b (intrachain scattering between two neighbouring pyrrole rings) and c (the interplanar spacing between the polypyrrole chains) are in agreement with those reported in the literature for PPY(TSO) [13, 14]. The parameter a which is related to the interchain spacing including TSO$^-$ anions is in our case smaller than the reported values [13, 15], because of the different orientation of these anions between the chains.

The inset of Fig. 7 shows $N_{eff}(\omega)$ for PPY(TSO) samples 1–4. These spectra show different frequency distributions of the oscillator strength of the conduction electrons in these samples. A major difference between samples 1 and 3 can be observed. The slower increase of $N_{eff}(\omega)$ for sample 1 indicates a greater structural disorder in this sample.

If we consider the polypyrrole sample as a two-phase system with high-conducting and low-conducting regions, the optical conductivity spectra will contain the contribution from the both phases. We consider that the high-conducting regions have a lower defects concentration and a more ordered structure as compared with the low conducting regions. The relative extensions of the ordered and disordered regions depend on the electrochemical deposition conditions [16]. Among the doping ions that we used, TSO$^-$ ions especially can strongly influence the structure of the electropolymerized polypyrrole. That explains the large variation of dc conductivity values as
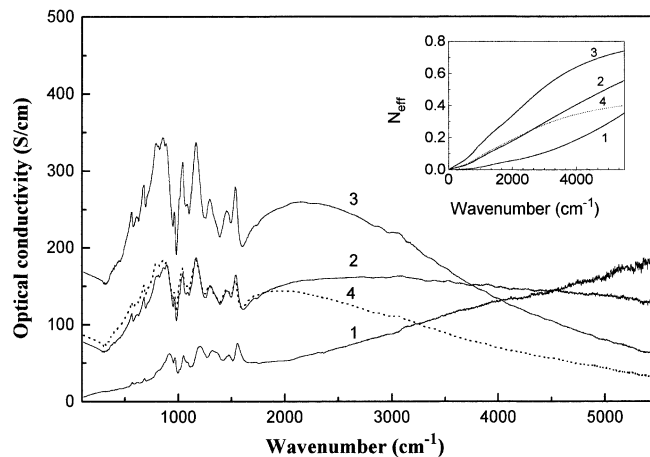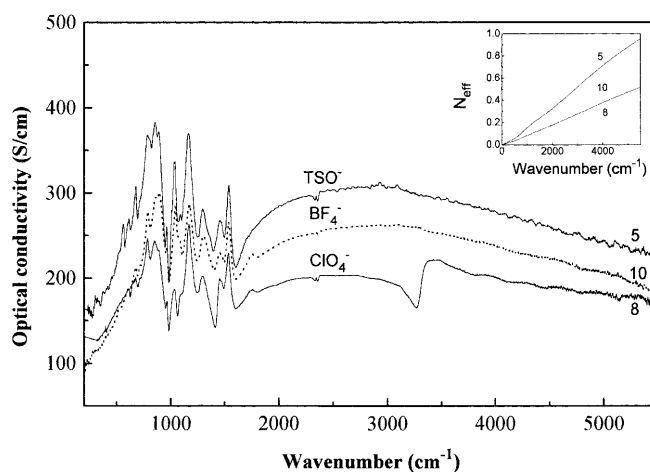
well as reflectance spectra obtained for PPY(TSO) electrochemically prepared in different conditions. Interchain hopping is the dominant charge transport mechanism in the low-conducting, disordered regions and contributes strongly to the measured σ_{dc}. The optical conductivity is more strongly influenced by the intrachain transport process rather than the slower interchain hopping process.

3 Conclusion

The effects of some relevant parameters – the electrolyte, the electropolymerization current density, and the film thickness – on the reflectance spectra of polypyrrole films were reported. Significant effects were observed especially for TSO$^-$-doped polypyrrole films. The reflectance increases with the decrease of the electropolymerization current density and film thickness.

The non-metallic behaviour of the dielectric function for the investigated polypyrrole samples is determined by the

disorder-induced localization of the carriers. Shorter deposition times and lower current density for the polymerization yield better conditions for a reduction of the structural disorder in the polypyrrole films.

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