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Polymer 44 (2003) 7809–7819

polymer

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Poly(*o*-toluidine) as the matrix for incorporation of palladium species from $PdCl_2$ aqueous solutions

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Received 14 April 2003; received in revised form 8 October 2003; accepted 17 October 2003

Abstract

Reactivity of poly(*o*-toluidine) in the emeraldine base form (POT) and protonated with HCl (POT/HCl) in $PdCl_2$ aqueous solutions of various HCl concentrations has been studied. Using elemental analysis, FTIR, UV–Vis, XPS and EXAFS spectroscopies as well as XRD and SEM it has been established that POT/HCl is more reactive than POT. The course of reactions is influenced by the type of the $PdCl_2$ solution. Thus, protonation of POT with incorporation of palladium (II) chloro–and/or aquachloro–and/or chlorohydroxycomplexes counterions is the main process occurring in the $PdCl_2$ solutions of higher HCl concentration. A redox reaction resulting in the oxidation of the polymer chain with simultaneous formation of metallic palladium takes place in the $PdCl_2$ solution of lower HCl concentration. POT/HCl shows enhanced reducing properties with respect to POT. Lowering of the protonation level (i.e. some deprotonation) of POT/HCl has been also observed. Coordination of palladium (II) ions by nitrogen atoms of the polymer chain can be also postulated.

Keywords: Poly(*o*-toluidine); Palladium; Polyaniline derivatives

1. Introduction

Since the discovery that polyaniline (PANI) becomes conductive upon simple acid treatment (often called protonation) [1] a great progress has been made in the synthesis and applications of this polymer. In particular, the most serious drawback in the applications of PANI, i.e. lack of processability has been overcome. This has been achieved either by protonation with appropriate functional acids or by derivatization of the polymer chain. The latter approach involves incorporation of substituents replacing hydrogen atoms either at nitrogen atoms or in the aromatic rings of the polymer.

Poly(*o*-toluidine) (POT) is a PANI derivative which contains the $-CH_3$ group in the *ortho* position with respect to nitrogen atoms. Among the ring-substituted PANI derivatives, POT has been probably the most frequently studied. Even though its conductivity in the protonated state is usually lower than that of PANI [2] it is soluble in popular organic solvents [3] and shows interesting electrooptical properties which make it suitable for use as an electrochromic material [4].

Due to electron-rich, conjugated nature of its chain, POT should readily react with transition metal ions which are good electron acceptors. Although polymer–transition metal systems are promising materials for a number of applications (e.g. as catalysts and sensors) there are only a few reports on incorporation of transition metals into POT. Based on UV–Vis and cyclic voltammetry studies Hirao et al. proposed that Pd [5], Pd–Cu bimetalic system [6] and

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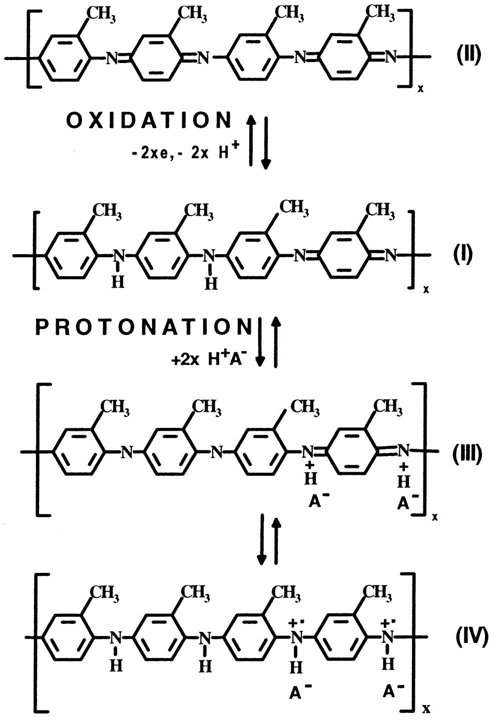
doi:10.1016/j.polymer.2003.10.036

V [7] form complexes with POT imine nitrogen atoms in organic solvents. POT acting as a redox-active ligand for palladium under oxygen was demonstrated to catalyze the Wacker oxidation of 1-decene [8].

The present work is devoted to the investigations of POT–palladium systems prepared in $PdCl_2$ aqueous solutions containing HCl of various concentrations. Several chemical reactions between POT and Pd^{2+} ions can take place in the experimental conditions studied. They are as follows:

- *Protonation of the polymer*. This reaction is presented in Scheme 1. Protonation of POT (I) results in the formation of a salt (III) in which the polymer backbone is positively charged and dopant anions (A^-) are incorporated into the system. Imine nitrogen atoms (=N–) present in the quinoid polymer units are protonated preferentially. An internal redox reaction leads to the tranformation of structure (III) into the polysemiquinone radical (IV), often called 'polaron lattice'. Since all the $PdCl_2$ solutions were acidic, protonation was the first process to be considered in the POT–palladium systems studied. Both, Cl^- and palladium-containing anions, such as $[PdCl_4]^{2-}$, $[PdCl_3(H_2O)]^-$, $[PdCl_3(OH)]^{2-}$ present in the solutions could act as dopant anions in the protonation reaction.
- *Redox processes*. POT can be oxidized as depicted in Scheme 1. In this reaction benzenoid units of POT (I) containing amine nitrogen atoms (–NH–) are oxidized into the quinoid units with imine nitrogen atoms (=N–). In such a way, fully oxidized POT (II) is formed. Intermediate oxidation states between (I) and (II) are, however, also possible. It can be expected that Pd^{2+} ions in the $PdCl_2$ solutions studied can serve as the oxidizing agent for POT. Hence, oxidation of POT should be accompanied by the formation of Pd^0.
- *Coordination of Pd^{2+} by nitrogen atoms of POT*. This reaction would result in the formation of the Pd–N bond.



Scheme 1.

Our preliminary studies carried out using vibrational spectroscopic methods (FTIR and Raman) showed that POT is less reactive than PANI towards palladium (II) species existing in $PdCl_2$ aqueous acidic solutions [9]. In this work, we describe the detailed investigations of POT–palladium systems using various experimental techniques, such as IR, UV–Vis, X-ray photoelectron and X-ray absorption spectroscopies as well as X-ray diffraction, scanning electron microscopy, microanalysis and conductivity measurements. In the studies, POT in the emeraldine base form and POT protonated with HCl (POT/HCl) have been used as the starting materials for incorporation of palladium species. The aim of the work has been to elucidate the influence of the type of the $PdCl_2$ solution on the chemical processes taking place in the systems as well as to verify the impact of the protonation of POT on these reactions.

It should be noted that the understanding of chemical reactions proceeding in a given system is a key step in the design of materials which exhibit desired composition and properties. Therefore results of the present work seem to be of fundamental importance for controlled preparation of POT–palladium and, more generally, conjugated polymer–transition metal systems for a variety of applications.

2. Experimental

2.1. Materials preparation

POT in the emeraldine base form was prepared using the procedure known for the synthesis of PANI [10]. *o*-Toluidine (0.96 mol) was oxidized with ammonium peroxodisulphate (0.24 mol) in 1.5 M HCl at 0 °C. POT hydrochloride thus obtained was washed with 1.5 M HCl and subsequently deprotonated at room temperature in 0.3 M aqueous ammonia solution for 24 h. Then POT base was filtered, washed with methanol and dried in dynamic vacuum till constant mass (~48 h). A part of this polymer was reprotonated in 1 M HCl in order to obtain fully protonated POT hydrochloride (POT/HCl) powder.

POT and POT/HCl–palladium systems were prepared by suspending polymer powders in the appropriate $PdCl_2$ solution in hydrochloric acid and stirring the suspension at room temperature till the concentration of Pd in the solution did not change (~27 h). The starting ratio of the polymer unit (calculated as $C_{28}H_{34}N_4$) to Pd moles in the reactions was equal to 1:2.

$PdCl_2$ solutions as well as POT–Pd and POT/HCl–Pd samples prepared together with their notations are given in Table 1. It should be noted that the composition of the $PdCl_2$ solutions was selected in such a way that the concentration of $PdCl_2$ was constant (4.6×10^{-3} M) while the concentration of HCl varied. Consequently, different palladium (II) chlorocomplexes dominated in the solutions. UV–Vis spectra interpreted according to Ref. [11] showed that $[PdCl_2(H_2O)_2]$ ($\lambda_{max} = 420$ nm), $[PdCl_4]^{2-} + [PdCl_3(H_2O)]^-$ ($\lambda_{max} = 465$ nm) and $[PdCl_4]^{2-}$ ($\lambda_{max} = 474$ nm) were the main complexes in the PdLA, PdMA and PdHA solutions, respectively.

Additionally, thin films of POT on quartz plates were prepared by evaporation of its solution in methylene chloride (0.1 wt%). Some of the films were treated with 1 M HCl solution in order to obtain films of POT/HCl. Both types of films were immersed in the appropriate $PdCl_2$ solution and studied using UV–Vis spectroscopy,

Table 1
Notations of $PdCl_2$ solutions and polymers–Pd samples studied in the work

$PdCl_2$ solution		Polymers–Pd samples prepared in the relevant $PdCl_2$ solution from	
HCl concentration (M)		POT	POT/HCl
0.66×10^{-3}	PdLA	BPdLA	SPdLA
0.1	PdMA	BPdMA	SPdMA
1.0	PdHA	BPdHA	–

LA, MA, HA stand for 'lowest', 'medium' and 'highest' acid concentration, respectively. In the whole work the abbreviation POT denotes the base polymer, whereas POT/HCl means POT protonated with HCl. B and S denote 'base' (i.e. POT) and 'salt' (i.e. POT/HCl)-derived samples, respectively.

2.2. Materials characterization

Determination of the contents of palladium in the $PdCl_2$ solutions during synthesis of POT–Pd and POT/HCl–Pd systems as well as in the POT–Pd and POT/HCl–Pd samples was carried out colorimetrically using the reaction of Pd^{2+} ions with KI [12]. Before analysis, the POT–Pd and POT/HCl–Pd samples were dissolved in $HClO_4/HNO_3$ mixture.

FTIR measurements in the MIR range (400–4000 cm^{-1}) were performed in a transmission mode on a BioRad FTS60v spectrometer using KBr pellet technique. The resolution of the IR measurements was equal to 4 cm^{-1}.

UV–Vis spectra in the range of 190–1100 nm were recorded on a Hewlett–Packard HP 8453 spectrophotometer equipped with a diode array detector.

XPS measurements were carried out using a VSW Manchester equipment and Al Kα radiation (1486.6 eV, 200 W). Operating pressure in the analytical chamber was less than 5×10^{-8} mbar. Carbon C1s photoelectron peak originating from C–H or C–C group fixed at binding energy (BE) equal to 284.6 eV was used for calibration. XPS spectra were decomposed into component peaks using the procedure described earlier [13].

Scanning electron microscopic (SEM) and X-ray microanalysis investigations were carried out on a Philips XL-30 microscope equipped with the EDS system. Point analyses of Cl and Pd contents in the samples were performed.

X-ray diffraction studies were carried out on a Seifert XRD 7 diffractometer using nickel-filtered Cu Kα radiation.

The X-ray absorption spectra at the Pd K edge were measured for POT–Pd samples as well as for the reference compounds: Pd foil, PdO, $[Pd(NH_3)_4]Cl_2$ and $PdCl_2$ in the transmission mode at room temperature at the station X1 of the synchrotron laboratory HASYLAB in Hamburg. The photon energy range from 24,100 to 25,200 eV was used in the experiments. In each measurement, absorption spectrum of a specimen was recorded simultaneously with that of Pd metallic foil which was used for calibration of the photon energy scale. Extended X-ray absorption fine structure (EXAFS) of POT–Pd samples and reference compounds were extracted in a standard way and compared with theoretical model ones using the WINXAS 2.1 program [14]. Theoretical phase and amplitude functions for Pd–O, Pd–Cl and Pd–Pd atomic pairs were calculated by the FEFF code [15].

Conductivity was measured on pressed pellets of the samples using a standard four-probe method.

3. Results and discussion

3.1. Studies of POT–Pd systems using various experimental techniques

3.1.1. Chemical analysis: contents of palladium in the POT matrix

We have found that in all the cases the amount of palladium incorporated into the polymers has been significantly lower than that in the starting $PdCl_2$ solution. The content of palladium in the POT matrix has always reached a certain maximum level (y_{max}, Table 2) with the value dependent on both, the type of the starting polymer (base or protonated) and the type of the $PdCl_2$ solution. Generally, values of y_{max} have been higher when POT/HCl has been the starting polymer. Among POT-derived samples, BPdMA

Table 2
Maximum palladium contents (y_{max}) in the POT–Pd and POT/HCl–Pd samples. y_{max} is expressed as the number of Pd moles per polymer unit (calculated as $C_{28}H_{34}N_4$)

Sample	y_{max}	Sample	y_{max}
BPdLA	0.32	SPdLA	0.85
BPdMA	0.52	SPdMA	0.62
BPdHA	0.32	–	–

shows the highest y_{max}. In contrast, y_{max} for SPdLA is higher than that for SPdMA.

Value of y_{max} can be treated as the measure of the overall reactivity of POT and POT/HCl towards palladium (II) species in the experimental conditions studied. Thus, it can be concluded that POT/HCl is more reactive than POT. This may be partly due to more hydrophilic properties of the protonated polymer than the base one which facilitates reactions proceeding in aqueous $PdCl_2$ solutions. A strong competition between Cl^- and palladium (II) complex anions acting as counterions in the protonation of POT is the most probable reason for low reactivity of POT in the PdHA solution. On the other hand, low acidity of the PdLA solution ($pH = 3.2$) limits protonation of the polymer. This explains low reactivity of POT under these conditions and suggests that other ways of palladium incorporation, such as redox processes or coordination dominate in the systems.

3.1.2. FTIR spectroscopy and conductivity measurements

Middle infrared range (MIR) spectra show protonation of the POT chain in most samples containing palladium. The BPdLA sample is the only exception. Its spectrum is almost identical with that of the starting polymer (Fig. 1). Slight difference in both spectra can be observed exclusively in the relative intensity of the bands at 1492 and 1598 cm^{-1}. These bands are related to the reduced (C–C stretching vibrations in the benzenoid units) and oxidized (C–C combined with C=N stretching vibrations of the quinoid units) moieties of POT, respectively [16,17]. Hence, slightly higher intensity ratio of the 1598 cm^{-1}/1492 cm^{-1} bands in the spectrum of the sample containing palladium than in that of the starting polymer may be attributed to some oxidation of the POT chain. Oxidation degree indicated by MIR is, however, low. Thus, MIR studies confirm low reactivity of POT towards palladium (II) species in the PdLA solution.

The spectra of BPdMA and BPdHA have been presented in our previous work [9]. In this paper, the spectra of POT/HCl-derived samples will be discussed in more detail.

MIR spectrum of the staring POT/HCl (Fig. 2) is similar to that reported in Ref. [16] for POT highly protonated with HCl. In particular, it shows a broad absorption centered at ~1200 cm^{-1} on which the bands at 1108, 1172, 1262 cm^{-1} due to bending modes of the ring CH groups as well as at 1216 and 1321 cm^{-1} assigned to C–N stretching vibrations [16,17] are superimposed. The bands originating from the benzenoid and quinoid rings at 1488 and 1592 cm^{-1}, respectively, are less intense than in the spectrum of POT (Fig. 1) which is consistent with structural changes of the polymer chain caused by protonation (formation of the delocalized charged units). A new band at 1550 cm^{-1} is most probably due to the C=N stretching vibrations shifted to lower wavenumbers upon protonation and thus resolved from the ring C–C stretching. Such shift has been observed in the spectra of POT protonated with $HClO_4$ and HBF_4 [17]. Although the authors of Ref. [17] have not recorded this band in the spectrum of POT/HCl, it is clearly seen in the spectrum presented in Ref. [16]. It can be also identified in the second derivative of the spectrum of POT/HCl protonated to lower extent whose envelope does not contain this band well resolved [9].

Upon incorporation of palladium into POT/HCl the band at 1592 cm^{-1} markedly increases with respect to that at 1492 cm^{-1}. The increase is higher in the case of the SPdLA sample than in the SPdMA one. This may be due to some deprotonation of POT/HCl or to the oxidation of the polymer, more pronounced in the PdLA solution.

Changes in relative intensities of the bands between 1000 and 1320 cm^{-1} in the spectra of the POT/HCl–Pd samples seem to indicate lower protonation level of these samples than that of the starting polymer. The changes are particularly significant in the case of the SPdLA sample. The band at 1172 cm^{-1} has shifted to 1157 cm^{-1}, i.e. to its position in the spectra of the samples protonated to a lower degree [9]. The band at 1327 cm^{-1} is the most intense one in this region (Fig. 2) which resembles the spectrum of POT base (Fig. 1). Additionally, the band at 1550 cm^{-1} has disappeared from the spectrum. Hence, partial deprotonation of POT/HCl in the PdLA solution can be postulated. Deprotonation of polypyrrole doped with chloride ions under these conditions has been also observed [13].

In the spectrum of the sample prepared in the PdMA

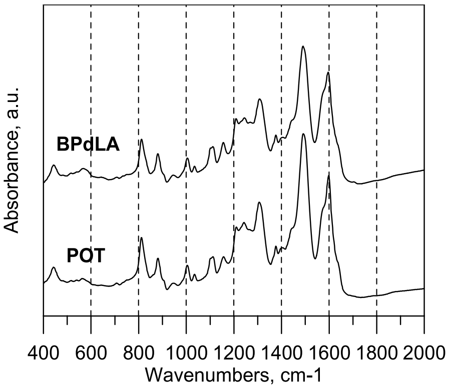


Fig. 1. MIR spectra of POT and BPdLA samples.

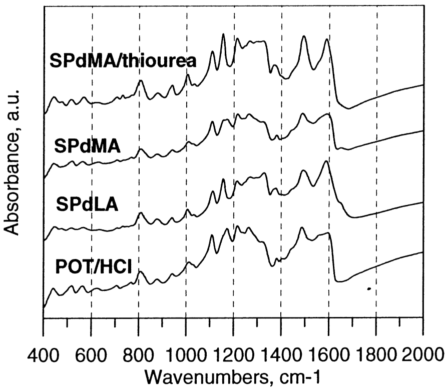


Fig. 2. MIR spectra of POT/HCl, POT/HCl-derived samples and SPdMA sample after treatment with a 5 wt% thiourea solution in 0.05 M HCl.

solution, a weak band at 1650 cm^{-1} is seen (Fig. 2). In this spectral range deformational modes of protonated N^+H groups are located [18]. This band disappears from the spectrum upon treatment of the sample with a thiourea solution which, similarly to other reports [19], has proved to remove all palladium from the sample (verified by XPS). This demonstrates that the band at 1650 cm^{-1} is connected with the incorporation of palladium (II) dopant anions into the POT matrix.

Conductivity measurements corroborate that in the $PdCl_2$ solutions a partial deprotonation of POT/HCl takes place. The results are collected in Table 3. Due to deprotonation, conductivity of POT/HCl drops to a lower extent after treatment with the PdMA solution (SPdMA sample) and almost four orders of magnitude after the PdLA solution (SPdLA sample). This is consistent with the MIR spectra which show lower protonation level of the SPdLA sample than the SPdMA one. It is also worth noting that the conductivity of our POT/HCl (9.2×10^{-3} S/cm, Table 3) is close to the value reported in the literature (10^{-2} S/cm) [2].

3.1.3. UV–Vis spectroscopy

UV–Vis spectra of POT and POT–Pd samples are shown in Fig. 3, whereas those corresponding to POT/HCl and POT/HCl–Pd samples are shown in Fig. 4.

POT exhibits two absorption maxima in the UV–Vis spectra: at 312 nm and at 592 nm (Fig. 3). Similarly to the spectra of PANI [20,21], they can be ascribed to $\pi-\pi^*$ transitions centered on benzenoid rings and the excitonic states resulting from electron transfer from benzenoid to quinoid rings, respectively. Upon treatment of POT with PdMA and PdHA solutions the maximum at 592 nm disappears, while a new maximum at ~400 nm as well as a broad one at 880 nm (PdMA solution) and a characteristic tail starting at ~600 nm extending into NIR (PdHA solution) show up. These maxima can be ascribed to the optical absorption of the protonated polymer [20,21]. Hence, the spectra prove protonation of POT in both $PdCl_2$ solutions.

Additionally, in the spectrum of the BPdHA sample the absorption maximum at 295 nm is seen. This band does not appear in the spectrum of POT/HCl and it disappears after deprotonation of the sample in aqueous ammonia solution. Clearly, this peak is connected with the presence of palladium counterions in the BPdHA sample. Since $[PdCl_4]^{2-}$ gives an intense band at 291 nm in the solid state [22], it can be concluded that this absorption maximum corresponds to $[PdCl_4]^{2-}$ acting as the counterion in the BPdHA sample.

Table 3
Conductivity values of POT/HCl as well as SPdMA and SPdLA samples

Sample	Conductivity (S/cm)
POT/HCl	9.2×10^{-3}
SPdMA	1.5×10^{-3}
SPdLA	9.3×10^{-7}

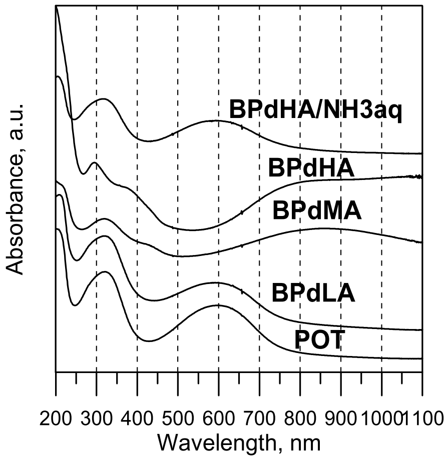


Fig. 3. UV–Vis spectra of POT and POT-derived samples. The BPdHA/NH_3 aq. sample was obtained after treatment of the BPdHA sample with 0.3 M aqueous ammonia solution.

In accordance with MIR studies, in the spectrum of the BPdLA sample the absorption maxima corresponding to the protonated polymer have not been observed. Instead, apart from the bands at 322 and 592 nm, a weak shoulder at 284 nm can be seen. A meaningful broadening of the 592 nm maximum at the shorter wavelength side in comparison with the spectrum of the starting polymer can be also observed. Since in the spectrum of the oxidized PANI the bands at 270, 320 and 560 nm have been recorded [20], it can be concluded that the shoulder at 284 nm as well as the broadening of the band at 592 nm result from a partial oxidation of POT in the PdLA solution. This again suggests that the redox process occurs in this solution.

When the spectra of POT/HCl–Pd samples are compared with that of POT/HCl (Fig. 4) it is seen that they all contain the broad band at around 800 nm corresponding to the protonated polymer. However, in the case of POT/HCl this band shows a tail which extends into NIR region, whereas in the spectra of POT/HCl–Pd samples it is more localized. Appearance or disappearance of the absorption tail in the UV–Vis spectra of PANI has been explained by changes in

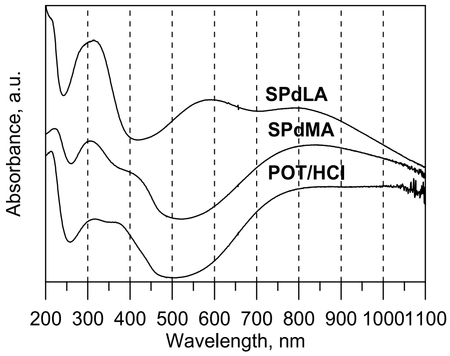


Fig. 4. UV–Vis spectra of POT/HCl and POT/HCl-derived samples.

conformation of the protonated polymer chain [23]. This suggests that upon incorporation of palladium species conformational changes of the POT chain occur. The spectrum of SPdMA sample is typical of protonated POT and is fairly similar to that of the sample synthesized from POT in the same conditions (BPdMA). The spectrum of SPdLA sample shows that, apart from the protonated phase, the oxidized one which gives absorption maxima at 580 and 284 nm exists in the system. The signs of oxidation of the polymer are remarkably stronger in this spectrum than in that of the corresponding sample prepared from POT. This implies stronger reducing properties of POT/HCl than those of POT.

It is interesting to compare our UV–Vis results with those reported by Hirao et al. for POT–Pd systems [5]. These authors have found that treatment of POT with various palladium(II) compounds ($Pd(OAc)_2$, $PdCl_2(MeCN)_2$ and a complex containing pyridinecarboxyamide and acetonitrile as ligands) in a solution in tetrahydrofuran is accompanied by the shift of the polymer excitonic band from 590 to ~700 nm. The shift value depends on the palladium compound used and on the amount of Pd ions introduced into the polymer matrix. This shift has been attributed to the coordination of palladium to POT imine nitrogen atoms. If it is assumed that the bond formation between Pd and POT nitrogen atoms in aqueous $PdCl_2$ solutions results in similar change in the UV–Vis spectrum then in our systems the Pd–N bond can be present in the samples which show broad absorption maxima at higher wavelengths, i.e. the protonated ones (BPdMA, BPdHA, SPdLA, SPdHA). However, in none of their spectra a well-resolved maximum which could be ascribed to the coordination of the polymer chain to Pd ions is seen. It can be only proposed that the 'coordination band' contributes to the broad maximum due to protonation. This may mean that in these samples the fraction of palladium ions involved in the coordination with POT nitrogens is too low to influence the UV–Vis spectrum significantly. Similar conclusion concerns the BPdLA sample in which—as indicated by UV–Vis as well as MIR studies—the polymer chain is partially oxidized and some of Pd^{2+} ions which could participate in coordination are reduced to Pd^0 (established by XRD and other studies described in the following sections). Hence, the UV–Vis investigations of our POT–Pd and POT/HCl–Pd samples do not exclude the Pd–N bond formation. They indicate, however, that in the $PdCl_2$ aqueous solutions the reactions of POT and POT/HCl other than coordination to palladium ions dominate.

3.1.4. XPS

XPS is a useful tool in the studies of POT–Pd systems. N1s spectra make it possible to determine changes occurring in the polymer chain upon incorporation of palladium species. Analysis of Pd3d and Cl2p spectra provides information on the way of palladium bonding and the type of counterions in the protonated samples.

XPS data for all the samples studied are collected in Table 4. Pd3d spectra recorded for selected samples are presented in Fig. 5.

N1s spectra contain four peaks corresponding to amine (–NH–), imine (–N=) and charged (i.e. protonated, $-N^+=$) nitrogen atoms which have been assigned according to Kang et al. [24]. When the proportions of the component peaks in the N1s spectra of the palladium-containing samples are compared with those of the starting polymers the following processes can be postulated to take place in the investigated systems:

1. Oxidation (–NH– groups transform into –N= with the appropriate changes in the shares of the N1s component peaks) and a slight protonation (–N= groups transform into to $-N^+=$ to a little extent) of POT in the PdLA solution; oxidation being the dominant reaction.
2. Protonation of POT in the PdMA and PdHA solutions.
3. Oxidation and partial deprotonation (transformation of $-N^+=$ groups to –N=) of POT/HCl in the PdLA solution.
4. Partial deprotonation of POT/HCl in the PdMA solution.

Thus, conclusions based on the N1s spectra are consistent with those based on MIR and UV–Vis spectroscopies.

The best fit of the Pd3d spectra in the case of POT–Pd and POT/HCl–Pd samples has been obtained when one $Pd3d_{5/2-3/2}$ doublet corresponding to Pd^0 component (binding energy, BE $Pd3d_{5/2} = 335.2$ eV) [25] and two

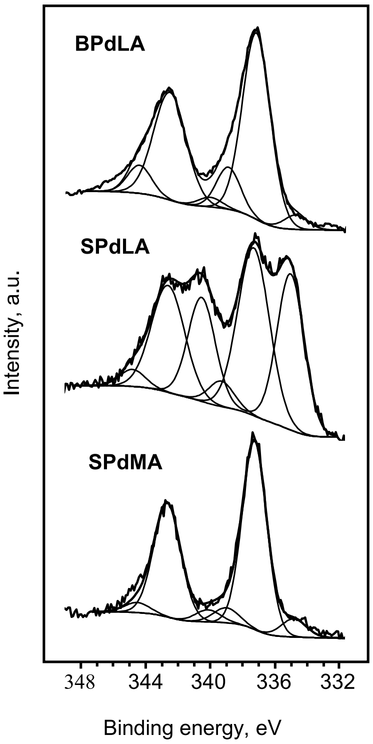


Fig. 5. Pd3d XPS of selected samples.

Table 4
Shares, binding energies and line width (full width at half maxiumum, FWHM) of components obtained after decomposition of XPS spectra of the samples studied

Sample	XPS data: shares (%)								
	Nis			$Cl2p_{3/2}$			$Pd3d_{5/2}$		
	−N=	−NH−	$-N^{+}=$	Cl^{-}	Cl^{*}	−Cl	Pd^{0}	Pd^{2+} in Pd−Cl, PdO	Pd in complexes
POT	30	58	12	–	–	–	–	–	–
BPdLA	40	45	15	50	39	11	5 (1.80[a])	77 (1.99)	18 (1.80[a])
BPdMA	21	57	22	80	15	5	5 (1.80[a])	84 (1.77)	11 (1.80[a])
BPdHA	12	62	26	83	14	3	2 (1.80[a])	87 (1.81)	11 (1.80[a])
POT/HCl	6	63	31	17	67	16	–	–	–
SPdLA	26	53	21	58	30	12	42 (1.95)	52 (2.27)	6 (1.80[a])
SPdMA	14	66	20	65	23	12	8 (1.80[a])	83 (1.73)	9 (1.80[a])
Binding energy (eV)	398.1	399.2	400.5, 402.1	197.6	198.8	200.3	335.2	337.5	339.3
FWHM (eV[a])	1.70			1.70					

[a] Values fixed for fitting.

$Pd3d_{5/2-3/2}$ doublets ascribed to Pd^{2+} components have been considered.

The highest proportion of Pd^{0} recorded for SPdLA sample shows that POT/HCl exhibits strong reducing properties towards Pd^{2+} ions in the PdLA solution. Pd^{0} has contributed to a little extent in the Pd3d spectra of other samples which for the BPdLA one is rather unexpected.

Precise assignments of the Pd^{2+} peaks are complicated. Therefore, preliminary experiments were performed using well-defined compounds. In these test measurements $PdCl_2$, PdO and $Pd[(NH_3)_4]Cl_2$ were used where the best fits of Pd3d spectra were obtained with $Pd3d_{5/2}$ BE of 337.9, 336.6, 339.5 eV and line width (FWHM) equal to 1.60, 1.64, 1.76 eV, respectively. On the basis these results as well as the literature data [25] one can conclude that the major Pd^{2+} component of the analyzed systems at $BE = 337.5$ eV represents palladium (II) chloro-, aquochloro- or chlorohydroxycomplexes. It can be supposed that these complexes play the role of counterions in the protonation of POT. Noticeable increase in this major $Pd3d_{5/2}$ line width for BPdLA and SPdLA samples may result from the contribution of palladium (II) oxide which exhibits $BE = 336.6$ eV (similar value was reported [26]). The oxide layer forms readily on the surface of metallic palladium grains. It should be noted that the presence of Pd^{0} in these samples has been unequivocally established in the XRD studies (see Section 3.1.5).

The second Pd^{2+} doublet (BE $Pd3d_{5/2} = 339.3$ eV) may signify formation of complexes between palladium ions and POT chain. BE of the Pd core level peaks in coordination compounds depends on the nature of ligands [25]. Nitrogen atoms in the palladium (II) coordination sphere shift the Pd3d BE to higher values. This has been reported for, e.g. $[Pd(pyridine)_2Cl_2]$ (BE $Pd3d_{5/2} = 339$ eV) [27], $[PdCl_2\text{-}(NH)_2(CH_2)_{12}CH_3)_2]$ (BE $Pd3d_{5/2} = 338.2$ eV) [28] as well as in our preliminary test analysis for $Pd[(NH_3)_4]Cl_2$. Thus, Pd^{2+} peak at high BE may be associated with the coordination of Pd^{2+} ions by nitrogen atoms of POT.

The Cl2p spectra contain three $Cl2p_{3/2-1/2}$ doublets. In POT/HCl two of them (Cl^{-} and Cl^{*}) can be assigned to chloride counterions, whereas the third doublet corresponds to chlorine covalently bound to the aromatic ring of the polymer (−Cl) [24]. In the case of the samples containing palladium, however, the intermediate doublet (Cl^{*}) can be partly due to Cl atoms in the Pd−Cl bond since $PdCl_2$ gives a Cl2p peak at the same position. Cl2p spectra suggest that in all POT−Pd and POT/HCl−Pd samples Cl^{-} are the prevailing counterions.

3.1.5. X-ray diffraction and SEM studies

XRD patterns of all the samples studied are shown in Figs. 6 and 7. XRD pattern of POT (Fig. 6) contains a broad halo centered ar $2\Theta = \sim 17°$ ($d = \sim 0.52$ nm) which demonstrates that the polymer has been totally amorphous. POT/HCl shows reflections at $2\Theta = 9$, 14, 25 and 27° ($d = 0.98$, 0.63, 0.36 and 0.33 nm, respectively) superimposed on an amorphous halo (Fig. 7). Such a diffraction pattern of POT/HCl has been attributed to its partially crystalline structure [29].

Upon incorporation of palladium species into both, POT and POT/HCl important changes in the diffraction patterns take place. The XRD reflections become less intense and broader than those of the starting polymers. In the case of POT/HCl a XRD peak at $2\Theta = \sim 9°$ disappears. Thus, the shape of diffraction patterns is governed by incorporated bulky palladium species which may cause polymer structural changes. Additionally, in the XRD patterns of BPdLA and SPdLA samples intense reflections at $2\Theta = 40°$ ($d = 0.22$ nm) and at $2\Theta = 46.6°$ ($d = 0.19$ nm) originating from crystalline metallic palladium particles are clearly seen. A weak reflection at $2\Theta = 40°$ due to crystalline metallic palladium is also visible in the XRD pattern of the SPdMA sample. The presence of metallic Pd in the samples confirms that the redox reaction between the polymers and palladium (II) ions occurs in the PdLA solution. Stronger reducing properties of POT/HCl than those of POT are

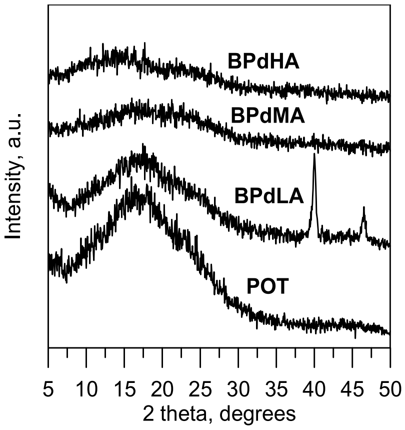


Fig. 6. XRD patterns of POT and POT-derived samples.

manifested by the appearance of metallic Pd in the PdMA solution as well.

SEM studies reveal that POT–Pd and POT/HCl–Pd samples exhibit similar surface morphology. They contain irregularly-shaped aggregates of various sizes ranging from 1 to 3 μm (Fig. 8). In backscattered electron (BSE) images white inclusions are visible in the samples prepared in the PdLA solution. They are significantly larger in the BPdLA sample (Fig. 8(B)) than in the SPdLA one (Fig. 8(D)). Using X-ray microprobe point analysis it has been found that in the white inclusions exclusively palladium has been present. In view of the XRD results which clearly show the existence of metallic Pd in these samples, it can be supposed that the white parts of the SEM images represent the metallic palladium particles. Hence, based on the SEM studies a better dispersion of Pd metal in the SPdLA sample than in the BPdLA one can be postulated. In the darker parts of BSE images of both, BPdLA and SPdLA samples the Cl:Pd atomic ratio has been within the range of 0.25–0.32. Most probably in these parts palladium (II) in the form of complexes is present. Oxygen contents has not been analyzed in our X-ray microprobe studies. It can be supposed, however, that oxygen-containing ligands have been the the main ones in the palladium (II) coordination sphere of the complexes incorporated into the BPdLA and SPdLA samples; Cl^- have constituted the minor ones.

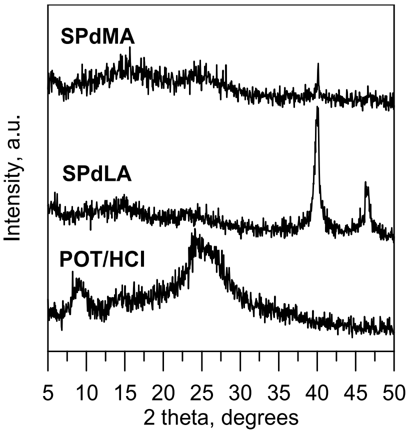


Fig. 7. XRD patterns of POT/HCl and POT/HCl-derived samples.

In the BSE images of the POT–Pd as well as POT/HCl–Pd samples prepared in the PdMA and PdHA solutions white inclusions have not been observed. The Cl:Pd atomic ratio within the range of 2–3 has been detected. This implies higher proportion of the Cl^- ligands in palladium (II) complexes introduced into the polymer matrices under the conditions of higher HCl concentration.

3.1.6. EXAFS spectroscopy

The X-ray absorption spectroscopic investigations of the local surrounding of palladium atoms make it possible to find out the types of neighbour atoms, distances and coordination numbers. Therefore, in the studies of POT–Pd samples this technique can be treated as complementary to XPS, XRD and SEM.

Two samples, namely BPdLA and BPdMA, have been selected for the EXAFS investigations. They showed similar, low contents of Pd^0 in XPS (Table 4) but only in the XRD pattern of BPdLA sharp reflections corresponding to crystalline metallic palladium particles were present (Fig. 6). Verification of this data seemed necessary.

In principle, four types of neighbour atoms, i.e. Cl (in palladium (II) chlorocomplexes present in POT as counter-ions), O (in palladium (II) chlorohydroxy- or aquochlorocomplexes and/or in palladium (II) oxide), N (in the coordination Pd–N bond) and Pd (in metallic particles) can appear around Pd atoms in POT–Pd samples.

Fourier transforms (FT) of EXAFS were calculated in the range k from 2.0 to 14.8 $Å^{-1}$, applying a Bessel window function and weighing factor k^3. In Fig. 9, the moduli of FT for two POT–Pd samples and reference compounds are compared. The Pd–Pd nearest shell is seen at $R = 2.5$ Å for the Pd metal. At $R = 1.9$ Å an FT peak originating from Pd–Cl distance is clearly visible in the $PdCl_2$ reference. The FT peak at $R = 1.6$ Å is characteristic for Pd–N shell in the $[Pd(NH_3)_4]Cl_2$ reference. A similar peak at $R = 1.6$ Å corresponds to Pd–O distance well separated in the case of PdO reference. In the R range from 2.5 to 3.5 Å three next neighbour shells Pd–Pd, Pd–Pd and Pd–O in PdO are overlapped. Strong differences in the FT shape for BPdLA and BPdMA samples are apparent. It can be noted, however, that in their FT curves a peak at $R = 1.6$ Å is present. It can be assigned to both, O and N neighbours which due to close distance values and similar scattering properties cannot be distinguished.

The least square fit in R space was done in the R range from 1.3 to 2.8 Å. First, fits were performed for experimental EXAFS data for reference compounds applying atom positions known from crystallographic data. Then fit parameters of references were used as starting values for fitting experimental EXAFS for POT–Pd samples. Parameters of best fits and residual factors are collected in Table 5. It is interesting to note that distances R_j fitted for Pd–O/N, Pd–Cl and Pd–Pd shells

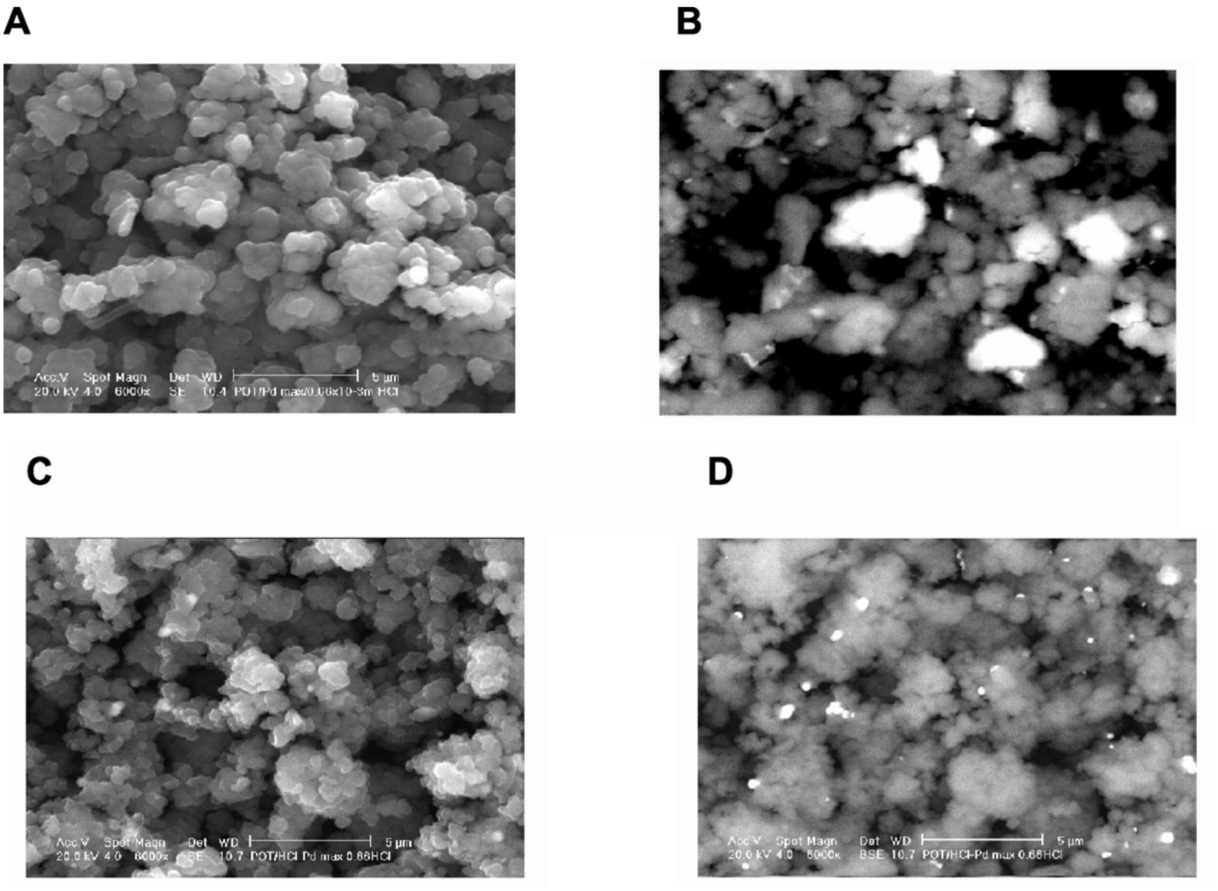


Fig. 8. SEM micrographs of: (A) and (B) BPdLA sample; (C) and (D) SPdLA sample. Images (A) and (C) have been obtained using secondary electrons and (B) and (D) back scattered ones.

in POT–Pd samples are almost identical with those in Pd references. In Fig. 10 moduli and imaginary parts of FT for theoretical EXAFS fits and experimental EXAFS data for both POT–Pd samples are presented. They agree very well which indicates that fitting was done properly.

The fitting procedure has revealed the differences between the BPdMA and BPdLA samples in more detail. Thus, in the case of BPdMA the proportion of Cl to O/N atoms in the palladium nearest neighbour shell is roughly equal to 3:1 (Table 5). Hence, chloride ions in various complexes (chloro-, chloroxydroxy-, aquochloro-, chloro-complexes containing N of POT chain as ligands) dominate in the surrounding of central palladium atom. Only a small amount of metallic palladium has been detected in this sample. Taking into account coordination numbers for the Pd complexes and Pd metal equal to 4 and 12, respectively, one can estimate from coordination numbers given in Table 5 that 97% of palladium is involved in complexes. The rest 3% of palladium remains in the form of metallic particles.

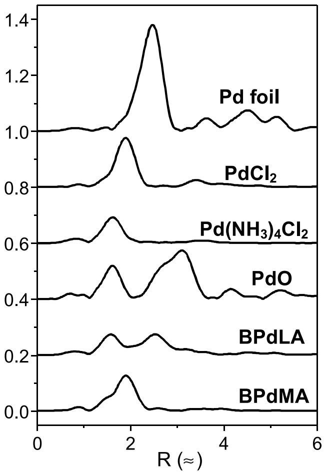


Fig. 9. Moduli of the Fourier transforms for reference compounds as well as BPdLA and BPdMA samples. Curves are shifted in the vertical scale for clarity.

In contrast, the amount of Pd metal in the BPdLA sample is significantly higher than in the BPdMA one. Oxygen and nitrogen atoms in Pd(II) complexes and oxygen atoms in palladium(II) oxide in the nearest neighbour shell at $R_j = 2.01$ Å around palladium atoms are dominating over other near neighbour shells in this sample. The presence of PdO is established, because of relatively high coordination number $N_j = 1.4$ of Pd neighbours in Pd–Pd$_{\text{oxide}}$ shell at $R_j = 3.05$ Å in comparison to $N_j = 4$ for similar shell in PdO reference. However, the next Pd–Pd$_{\text{oxide}}$ shell at R_j equal to about 3.42 Å is very weak, which means that in the

Table 5
Coordination numbers N_j, distances R_j and Debye–Waller factors σ_j^2 of the jth nearest neighbour shells around Pd and residual factor of the best fits of EXAFS data for Pd reference compounds and POT–Pd samples

Sample[a]	Neighbour	N_j	R_j (Å)	σ_j^2 (Å^2)	Residual factor (%)
PdO	O	4	2.02	0.0024	4.4
	Pd	4	3.03	0.0047	
	Pd	8	3.42	0.0050	
	O	8	3.73	0.0170	
$[Pd(NH_3)_4]Cl_2$	N	4	2.04	0.0027	4.5
$PdCl_2$	Cl	4	2.31	0.0034	3.3
Pd foil	Pd	12	2.74	0.0057	2.8
BPdMA	O/N[b]	1.1	2.01	0.0026	4.4
	Cl	2.8	2.31	0.0032	
	Pd_{metal}	0.3	2.73	0.0056	
BPdLA	O/N[b]	2.8	2.01	0.0036	2.8
	Cl	0.7	2.30	0.0032	
	Pd_{metal}	1.7	2.73	0.0056	
	Pd_{oxide}	1.4	3.05	0.0062	

[a] Structural data for PdO, $[Pd(NH_3)_4]Cl_2$, $PdCl_2$, Pd foil taken from Refs. [30–33], respectively.

[b] In view of similar distances and scattering properties of O and N atoms in the palladium neighbour shell both atoms can contribute into this peak.

BPdLA sample PdO exists in nanocrystalline form. Highly dispersed structure of the PdO species is the reason for the lack of its diffraction signal in the XRD pattern of this sample.

Most probably, PdO results from the surface oxidation in air of metallic palladium particles present in the BPdLA sample. If the oxide layer covers the Pd metal grains then the Pd metal signal may become poorly visible in XPS, which is a surface technique. In contrast, XRD and EXAFS provide information on the whole volume of the sample and are able to detect metallic Pd particles in spite of the oxide overlayer. This may explain the underestimated Pd^0 content in the XPS studies of the BPdLA sample.

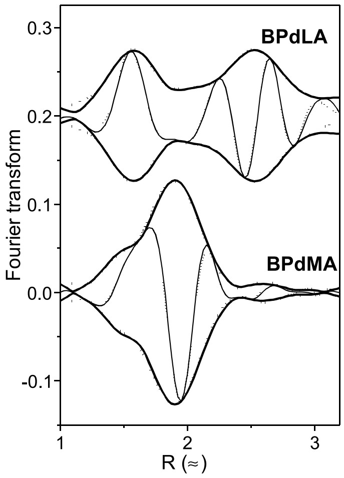


Fig. 10. Magnitude and imaginary part of the Fourier transform of experimental (solid lines) and theoretical (dotted lines) EXAFS for BPdMa and BPdLA samples.

One can estimate the composition of the BPdLA sample from coordination numbers given in Table 5: 14% palladium in Pd metal, at least 35% palladium in PdO and the rest of palladium in complexes.

3.2. Proposed explanation of the observed phenomena

Studies of POT–Pd and POT/HCl–Pd systems using various experimental techniques show that the reactions between the polymers and Pd^{2+} ions strongly depend on the HCl concentration in the $PdCl_2$ solution. Redox processes are particularly pronounced in the PdLA solution and the acid–base ones are the main ones in the PdMA and PdHA solutions. We suppose that this may be explained if the types of palladium (II) chlorocomplexes predominating in the $PdCl_2$ solutions studied are considered.

Thus, $[PdCl_2(H_2O)_2]$ prevails in the PdLA solution. Its reduction to Pd^0 yielding 2 Cl^- proceeds easily in the medium of low HCl concentration.

$[PdCl_4]^{2-}$ and $[PdCl_3(H_2O)]^-$ are dominating in the PdMA solution. They are difficult to be reduced in this acid concentration because $4Cl^-$ and $3Cl^-$, respectively, are formed in these reactions. Therefore, protonation of POT with Cl^- and palladium (II) aquo- and/or chlorohydroxy complexes counterions is the main proccess under these conditions.

Reduction of $[PdCl_4]^{2-}$, i.e. the dominant complex in the PdHA solution, is even more difficult in the solution of high HCl concentration. Therefore in this solution a redox process has not been observed. Protonation of POT with $[PdCl_4]^{2-}$ and Cl^- counterions has been the main one.

It is also worth noting that due to higher standard redox potential palladium (II) aquo- and aquochlorocomplexes are reduced more easily than palladium (II) chlorocomplexes (E^0 $[Pd(H_2O)_4]^{2+}/Pd = 0.99$ V and E^0 $[PdCl_4]^{2-}/Pd = 0.62$ V [34]).

Enhanced reducing properties of POT/HCl in comparison with those of POT can be explained by the fact that in the studies fully protonated POT has been used. In such polymer all imine nitrogen atoms are protonated. Therefore, the –NH– groups are the principal reaction sites. They undergo oxidation. POT/HCl is such a strong reducing agent that it is capable of reducing some Pd^{2+} to Pd^0 even in the unfavourable conditions (PdMA solution) whereas POT is not.

Partial deprotonation of POT/HCl has been observed in the PdLA and PdMA solutions. It may have been caused by $[PdCl_2(H_2O)_2]$ and $[PdCl_3(H_2O)]^-$ present in these solutions. H_2O in the Pd^{2+} coordination sphere is known to be easily replaced by other ligands [35], Cl^- from POT/HCl in this case.

4. Conclusions

When POT and POT/HCl are treated with $PdCl_2$

solutions of various HCl concentrations the following reactions take place in the systems:

1. Oxidation of the polymers with simultaneous reduction of a fraction of Pd^{2+} to Pd^0 in the $PdCl_2$ solution in 0.66×10^{-3} M HCl. POT/HCl is able to reduce some Pd^{2+} even in the $PdCl_2$ solution in 0.1 M HCl which means that its reducing properties are stronger than those of POT.
2. Protonation of the polymers with Cl^- and palladium(II) complexes containing Cl^-, OH^- and H_2O ligands acting as counterions in the $PdCl_2$ solutions in 0.1 and 1 M HCl.
3. Partial deprotonation of POT/HCl in the $PdCl_2$ solutions in 0.66×10^{-3} and 0.1 M HCl.

In all the cases, coordination of a part of incorporated Pd^{2+} ions by the polymers nitrogen atoms can be postulated.

The main reactions proceeding in the investigated systems are determined by the type of the palladium (II) chlorocomplexes prevailing in the $PdCl_2$ solutions.

Results of the studies can serve as the basis for controlled preparation of POT–palladium and, more generally, conjugated polymer–transition metal systems for a variety of applications.

Acknowledgements

EXAFS spectroscopic studies were supported by the IHP-Contract HPRI-CT-1999-00040/2001-00140 of the European Commission and by the Polish Committee for Scientific Research (KBN) through Grant No. 7T09A 137 21.

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