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Electropolymerization of chlorinated phenols on a Pt electrode in alkaline solution Part III: A Fourier transformed infrared spectroscopy study

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Abstract

FTIR spectroscopy was employed to investigate high molecular weight substances formed on a platinum electrode surface during the electrochemical oxidation of phenol and its chlorinated derivatives. Potentiodynamic (potential range from −0.80 V to 0.85 V vs SHE; scan rate 200 mV s^{-1}) and potentiostatic (at 0.78 V vs SHE) electropolymerization was used in alkaline solutions (1 M NaOH) containing 0.1 M of phenol, monochlorophenols, dichlorophenols, trichlorophenols and pentachlorophenol. The IR spectra of the corresponding monomers were recorded for the comparison. The FTIR spectroscopy studies revealed that the polymers formed under potentiodynamic and potentiostatic conditions are of aromatic nature (–C=C– stretching vibrations at 1450–1600 cm^{-1}), they have ether-linkages (=C—O—C= stretching vibrations at 1100–1300 cm^{-1}) and quinone groups (–C=O stretching vibrations at 1630–1800 cm^{-1} and –C—H out-of-plane bending at 760 cm^{-1}). The intensities of the hydroxyl group bands in most of the polymers are rather weak compared to those in the corresponding monomers. Vibrations at 2850–2960 cm^{-1}, which are present in most of the IR spectra of polymers formed under cyclic voltammetry conditions, correspond to the stretching vibrations of the sp^3 hybridized C—H bond and suggest that the cleavage of the benzene ring occurs to some extent during electrooxidation–electropolymerization of phenol and its chlorinated derivatives when reaching the potential of oxygen evolution (0.85 V vs SHE).

1. Introduction

It is commonly known that the electrooxidation of phenol and its derivatives generates phenoxy radicals on the electrode surface, which can be further oxidized or react with each other forming either ether- and quinone-type oligomeric or polymeric compounds [1–14]. The compounds of a high molecular mass rapidly deactivate the electrode and further oxidation slows down. The specific features of these polymeric tars are their low permeability and strong adhesion to the electrode [1, 4]. For characterization of these polymeric compounds spectroscopic methods are very useful, particularly Fourier transformed infrared (FTIR) spectroscopy.

Using infrared spectroscopy Dubois et al. found that poly-phenolic compounds produced in hydroalcoholic solutions have an excellent adherence to the metal surface, homogenity, hydrophobicity and stability [7, 15, 16]. Gatrell and Kirk used FTIR spectroscopy to analyse samples of polymers produced in acidic medium during electrooxidation of phenol. The authors found that the polymer contains a mixture of mostly directly linked phenol rings with some ether-linked rings [1, 2]. Glarum et al. [14], using several phenol derivatives, that is, 2,6-dimethylphenol (DMP), 2,4,6-trimethylphenol (TMP) and 4-*t*-butylphenol (TBP), obtained polymeric films on a rotating disk and platinum sheet electrodes in the NaOH medium. For the film derived from DMP the IR spectra confirmed a head-to-tail coupled structure [14].

The electropolymerization of phenolic compounds mainly occurs via the *ortho* and *para* positions and 1,2,4-, 1,2,6- and 1,2,4,6-polyphenol derivatives are formed [1–3, 5, 7, 8, 14]. However, in the case of 4-tertbutylphenol and 2,6-dimethylphenol, the favoured ring-ring coupling is prevented due to a steric hindrance caused by bulky tertbutyl and two methyl groups on one aromatic ring and the oxygen of the other. Therefore, a planar coupling predominates and high molecular weight ether-linked polymers are formed [2, 14]. The exceptions from the general polymerization routes are phenol derivatives with 2-, 4- and 6- positions occupied by groups or atoms other than hydrogen. 2,4,6-trimethylphenol (TMP) is one such derivative. It was reported that analogous radicals, as in the case of 2,6-dimethyl- and 4-tertbutylphenols, are formed in the course of TMP polymerization. These radicals are unstable and can isomerize to a quinone-methide intermediate by the loss of the hydrogen atom or to a hydroxybenzyl radical [14]. The polymeric product represents a dimeric analogue of polybenzyl ether with the aromatic groups coupled through the $-CH_2-O-$ links. Such a polymer could result from a quinone-methide addition to the phenoxide group terminating a polymer chain [14]. Polymerization does not occur when the 2-, 4- and 6- positions are occupied by bulky substituents. It was reported that 4-bromo-2,6-di-*t*-butylphenol and pentabromophenol cannot be oxidatively polymerized [17].

In the case of some chlorinated phenols, for example, pentachlorophenol, electropolymerization proceeds through the electrochemically generated radical-substrate coupling followed by elimination of the chloride ion [8]:

$$C_6Cl_5O^{\bullet} + C_6Cl_5O^- \rightarrow [C_6Cl_5OC_6Cl_5O]^{\bullet -} \quad (1)$$

$$[C_6Cl_5OC_6Cl_5O]^{\bullet -} \rightarrow C_6Cl_5OC_6Cl_4O^{\bullet} + Cl^- \quad (2)$$

In previous work we studied a Pt electrode fouling in alkaline solutions of chlorophenols by means of cyclic voltammetry [18] and the electropolymerization kinetics by means of EQCM [19]. It was shown that the electrode passivation is due to electropolymerization of chlorophenols and the fouling rate (decay in the anodic current during repetitive cycling over a potential range between hydrogen and oxygen evolution) is the highest for the *para*-substituted monomers [18, 19]. The monomer coupling through the ether links and dechlorination from the active *ortho* and *para* positions was assumed to occur according to the EQCM data [19]. The present work is aimed at FTIR spectroscopy studies of the electrooxidation–electropolymerization products for phenol and its chlorinated derivatives in alkaline medium on Pt in order to characterize qualitatively the high molecular weight substances formed on the electrode surface under the potentiodynamic and potentiostatic conditions applied in [18, 19].

2. Experimental details

A potentiostat PI-50-1 and a function generator PR-8 (Russia) were used to conduct the electrochemical measurements. Two digital voltmeters V7-43 (Russia) were connected to an IBM-PC through the IEEE-488 interface for the current–voltage data acquisition. A working Vinkler (Pt net-sheet) electrode (6 cm × 6 cm, real surface area 1736 cm^2), a Pt foil counter electrode (geometric area 2 cm^2) and an $Ag/AgCl/KCl_{sat}$. reference electrode (all potentials are referred to the standard hydrogen electrode (SHE)) were used for electrochemical measurements. A three-electrode electrochemical cell (~60 ml volume) was used for the measurements. The real surface area of the polycrystalline Pt electrode was found from the hydrogen monolayer adsorption charge on platinum in 0.5 M H_2SO_4 solution [20, 21]. The potential sweep rate in the potentiodynamic experiments was 200 mV s^{-1}. The range of the potential scan was from −0.80 to 0.85 V vs SHE. Typically up to five cycles in this potential region were applied for the potentiodynamic electropolymerization (except 20 cycles for pentachlorophenol due to low electropolymerization rate). The potentiostatic electropolymerization experiments were performed at 0.78 V vs SHE for 15 h.

The electrochemical experiments were performed in 1 M NaOH solution containing 0.1 M of phenol or chlorophenols (from Aldrich, Riedel-de Häen, Fluka) at 20 ± 1 °C. Ar gas was bubbled through the solutions during the measurements to remove oxygen. All the solutions were prepared using triply distilled water. Chemicals of pure and analytical grade were used.

The polymeric deposits formed on the electrode surface under potentiodynamic or potentiostatic conditions were rinsed with distilled water, immersed in 1 M NaOH solution to remove residues of the monomers, then again washed with water and finally dried in argon. The polymers were dissolved in 15 ml of chloroform. The solutions obtained were then concentrated to 10 μl, pipetted onto KBr discs, chloroform was evaporated and dry residues were analysed with a FTIR spectrometer BOMEM Michelson (ABB Bomem, USA) using 10 scans at 4 cm^{-1} resolution. A background subtraction was used to compensate the peaks caused by the CO_2, H_2O vapour and KBr absorbance.

3. Results and discussion

A Pt electrode of large surface area was used for oxidative potentiodynamic and potentiostatic electrochemical electropolymerization in order to collect a sufficient amount of the polymeric compounds. The IR spectra of the corresponding monomers were recorded to compare their characteristic vibrations with the IR spectra of the polymers formed during potentiodynamic and potentiostatic electropolymerization. The IR vibrations for the characteristic groups of the high molecular weight substances formed during eletropolymerization of phenol, monochlorophenols, dichlorophenols, 2,3,6-, 2,4,5-, 2,4,6-trichlorophenols and pentachlorophenol, and those of the corresponding monomers are presented in Tables 1–3. The IR spectra of the monomers and corresponding polymers, electrodeposited under potentiodynamic and potentiostatic conditions, are shown in Figures 1–4 (the CV and EQCM data for electropolymerization of corresponding phenols on Pt are reported elsewhere [18, 19]).

The comparison of the IR spectra of the monomers with the spectra of the corresponding polymers show several differences which may be referred to as the disappearance of the certain bands and an appearance of the new ones in the spectra (Figures 1–4). For instance, the bands in the range of 3200–3600 cm^{-1} (Tables 1–3) are present in the IR spectra of all monomers (Figures 1(a)–4(a)) while analogous bands in the spectra of the polymers are weak or entirely absent (Figures 1(b,c)–4(b,c)). One more difference between the IR spectra of the monomer and the corresponding polymer is an appearance of the bands

Table 1. Characteristic group vibrations of phenol, 2-chlorophenol monomers and corresponding polymers
arom: aromatic; quin: quinonic; sp^3–sp^3 hybridization; *g*: out-of-plane bending; *v*: stretching; *B*: in-plane bending.

Monomers and polymers	Frequencies of the characteristic vibrations of the monomers and polymers cm^{-1} [22–24]									
	arom. *g*(C—H)	quinon. *g*(C—H)	*v*(C—Cl) [25]	*v*(C—O)	*B*(C—O—H)	**v*(C═C)	*v*(C═O)	sp^3*v* *v*(C—H)	arom. *v*(C—H)	*v*(O—H)
Phenol (Fig. 1(a))	690, 753 [25]	–	–	1228	1367	1473, 1499, 1596	–	–	–	~3300
Poly-phenol (CV) (Fig. (1b))	–	754	–	1150–1270	1386	1450–1600	~1700	2850–2960	–	3100–3600
Poly-phenol (0.78 V, 15 h) (Fig. (1c))	–	754	–	1150–1270	1386	1450–1600	~1700	2850–2960	–	3100–3600
2-Chlorophenol (Fig. (1a))	749 [25]	–	1029, 1056	1127, 1199, 1251, 1291	1339	1452, 1480, 1585	–	–	3976, 3041	~3450
Poly-2-chlorophenol (CV) (Fig. (1b))	–	757	1058, 1061	1100–1300	–	1450–1600	~1650–1750	2850–2960	–	–
Poly-2-chlorophenol (0.78 V, 15 h) (Fig. (1c))	–	754	1054	1100–1300	–	1450–1600	~1650–1750	–	–	~3200–3600
3-Chlorophenol (Fig. (1a))	679, 771, [25]	–	1070, 1090	1100–1300	1321	1446, 1475, 1591	–	–	–	~3330
Poly-3-chlorophenol (CV) (Fig. (1b))	–	754	~1060	1100–1300	–	1450–1600	~1650–1750	2850–2960	–	–
Poly-3-chlorophenol (0.78 V, 15 h) (Fig. (1c))	–	754	~1060	1100–1300	–	1450–1600	~1650–1750	2850–2960	–	3400–3600
4-Chlorophenol (Fig. (1a))	825 [25]	–	1094	1127, 1199 1251, 1291	1339	1452, 1480, 1585	–	–	3076, 3041	~3450
Poly-4-chlorophenol (CV) (Fig. (1b))	–	755–760	~1100	1100–1300	–	1450–1600	~1650–1800	2850–2960	–	~3200–3600
Poly-4-chlorophenol (0.78 V, 15 h) (Fig. (1c))	–	755–760	~1100	1100–1300	–	1450–1600	~1650–1800	–	–	~3200—3600

* C—H (sp^3 hybridization) bending of the –CH_2 ir –CH_3 groups at 1450–1465 cm^{-1} [24], in the case of the polymers formed which have deeper oxidized products (with cleavage benzene or quinone ring) in their mixtures may be present.

in the region 2850–2960 cm^{-1} (Tables 1–3) in the IR spectra of most of the polymers (Figures 1(b,c)–4(b,c)) while these vibrations are completely absent in the spectra of the monomers (Figures 1(a)–4(a)). Another characteristic feature of the IR spectra of the polymers are vibrations at 1630–1800 cm^{-1} (Figures 1(b,c)–4(b,c) and Tables 1–3) which are not present in the monomer IR spectra (Figures 1(a)–4(a)). Furthermore, the IR spectra of the polymeric compounds exhibit a more or less sloped baseline for most of the samples (Figures 1(b,c)–4(b,c)). Such a sloped baseline in the spectra is probably due to small crystalline regions of various sizes in the sample, which scatter the infrared light to different degrees depending on the wavelength. The appearance of small crystalline regions of various sizes could be due to the presence of a variety of oligomers and polymers. The IR spectra of the polymers produced by electro-oxidation under potentiodynamic (Figures 1(b)–4(b)) and potentiostatic (Figures 1(c)–4(c)) conditions share almost the same characteristic vibrations. However, some differences also can be seen in the intensities of some vibrations. The most prominent difference is rather intense bands at 2850–2960 cm^{-1} in the IR spectra of polymers produced under CV oxidation conditions (Figures 1(b)–4(b)) compared to the corresponding vibrations in the IR spectra of polymers deposited potentiostatically (Figures 1(c)–4(c)). The latter vibrations are weak for most of the polymers deposited under potentiostatic conditions or are entirely absent (Figures 1(c)–4(c)).

The substitution pattern in the IR spectra of the monomers (Figures 1(a)–4(a)) could be easily distinguished by the out-of-plane bending vibrations of the benzene ring C—H bond which are seen in the region of 680–900 cm^{-1} [4, 22]. However, in most cases it is difficult to conclude concerning the substitution pattern of the corresponding polymers from the C—H bending vibrations since the bands in this region are weak and some polymeric compounds show a more or less sloped base line even after background subtraction (Figures 1(b,c)–4(b,c)). Moreover, vibrations characteristic of quinone-type compounds (═C—H bending) occur in the same region, and the presence of such compounds is supported by a stretching frequency of the C═O group at 1630–1800 cm^{-1}. Therefore, vibrations in the region of 680–900 cm^{-1} could be equally attributed to the benzene ring C—H bending as well as to quinone ═C—H bending in the mixtures of polymers formed.

Broad bands at 1100–1300 cm^{-1} (Tables 1–3) in the IR spectra of the polymers (Figures 1(b,c)–4(b,c)) are characteristic of an oxygen attached to an aromatic ring and can be attributed to ═C—O—C═ stretching vibrations [2, 4, 22] (taking into account the lack of an O—H vibration at 3200–3600 cm^{-1}). This suggests that during electropolymerization ether-linked polymers are formed. The presence of carbonyl group vibrations (1630–1800 cm^{-1}) along with ═C—H frequencies (~760 cm^{-1}) (Tables 1–3) in most of the polymers formed indicates that coupling through the C—C links also occurs, with

Table 2. Characteristic group vibrations of 2,3-, 2,4-, 2,5-, 2,6-, 3,4-, and 3,5-dichlorophenols monomers and corresponding polymers arom: aromatic; quin: quinonic; sp^3–sp^3 hybridization; _g_: out-of-plane bending; _v_: stretching; B: in-plane bending.

Monomers and polymers	Frequencies of the characteristic vibrations of the monomers and polymers/cm^{-1} [22–24]									
	arom. _g_(C—H)	Quinon. _g_(C—H)	_v_(C—Cl) [25]	_v_(C—O)	B(C—O—H)	*_v_(C—C)	_v_ (C—O)	sp^3_v_(C—H)	arom. _v_(C—H)	_v_(O—H)
2,4-Dichlorophenol (Fig. 2(a))	724, 815, 860 [25]	–	1053, 1096	1140–1300	1330	1406, 1479, 1584	–	–	3097	3300–3600
Poly-2,4-dichlorophenol (CV) (Fig. 2(b))	842, 867	759	1059	1100–1300	1360–1390	1410–1600	1640–1800	2850—2960	3089	3350–3540
Poly-2,4-dichlorophenol (0.78 V, 15 h) (Fig. 2(c))	844, 863	757	1059	1100–1300	–	1410–1600	1640–1800	–	3088	~3200–3650
2,3-Dichlorophenol (Fig. 2(a))	701, 740, 769 [25]	–	1047	1100–1310	–	1443, 1577	–	–	3085	3240–3440
Poly-2,3-dichlorophenol (CV) (Fig. 2(b))	–	761	1054	1100–1320	–	1420–1600	1630–1800	2850—2960	3018, 3076	3440–3530
Poly-2,3-dichlorophenol (0.78 V, 15 h)(Fig. 2(c))	–	759	1054	1100–1300	–	1447, 1574, 1596	1640–1800	2850–2960	3083	~3550
2,5-Dichlorophenol (Fig. 2(a))	801, 855, 899 [25]	–	1056, 1087	1130–1280	1340–1370	1426, 1492, 1580	–	–	–	3100–3600
Poly-2,5-dichlorophenol (CV) (Fig. 2(b))	808	759	1059, 1089	1100–1300	–	1450–1600	1650–1800	2850–2950;	–	–
Poly-2,5-dichlorophenol (0.78 V, 15 h) (Fig. 2(c))	808	758	1060, 1089	1130–1300	1370–1400	1472, 1577	~1720	2850–2960	3094	3300–3600
2,6-Dichlorophenol (Fig. 3(a))	713, 769, ~800 [25]	–	1066, 1098	1100–1280	1336	1449, 1467, 1577	–	–	3021, 3075	3250–3550
Poly-2,6-dichlorophenol (CV) (Fig. 2(b))	820–850	760	1069	1100–1300	–	1420–1600	1650–1800	2850–2960	3018, 3083	–
Poly-2,6-Dichlorophenol (0.78 V, 15 h) (Fig. 2(c))	790–850	758	1069	1100–1280	~1330	1446, 1479, 1574, 1600	1650–1800	2850–2960	3085	~3520
3,4-Dichlorophenol (Fig. 3(a))	657, 817, 844 [25]	–	1025	1131, 1227, 1270	1364	1433, 1475, 1596	–	–	–	3100–3400
Poly-3,4-dichlorophenol (CV) (Fig. 3(b))	–	759	1029, 1053	1120–1280	~1365	1410–1600	1650–1800	2850–2960	–	3200–3600
Poly-3,4-dichlorophenol (0.78 V, 15 h) (Fig. 3(c)	–	759	1030, 1056	1120–1280	~1370	1410–1600	1650–1800	2850–2960	–	3200–3600
3,5-Dichlorophenol (Fig. 3(a))	668, 805, 842 [25]	–	1101	1214, 1250, 1290	1370–1390	1430, 1463,1585	–	–	–	3050–3430
Poly-3,5-dichlorophenol (CV) (Fig. 3(b))	809, 841	760	1097	1210–1300	~1380	1430–1600	1630–1780	2850–2960	–	–
Poly-3,5-dichlorophenol, (0.78 V. 15 h) (Fig. 3(c))	811, 842	759	1097	1210–1300	–	1420–1600	1660–1750	2850–2960	3089	~3500

*C—H (sp^3 hybridization) bending of the –CH$_2$ ir–CH$_3$ groups at 1450–1465 cm^{-1} [24], in the case of the polymers formed which have deeper oxidized products (with cleavage benzene or quinone ring) in their mixtures may be present.

Table 3. Characteristic group vibrations of 2,4,6-, 2,4,5-, 2,3,6-trichlorophenols (TCP) and pentachlorophenol (PCP) monomers and corresponding polymers arom: aromatic; quin: quinonic; sp^3–sp^3 hybridization; *g*: out-of-plane bending; *v*: stretching; *B*: in-plane bending.

Monomers and polymers	Frequencies of the characteristic vibrations of the monomers and polymers/cm^{-1} [22–24]									
	*arom. *g*(C–H)	quinon. *g*(C–H)	*v*(C–Cl) [25]	*v*(C–O)	*B*(C–O–H)	†*v*(C=C)	*v*(C=O)	sp^3 *v*(C–H)	arom. *v*(C–H)	*v*(O–H)
2,4,6-TCP (Fig. 4(a))	729, 795, 860 [25]	–	1000	1164, 1220, 1277, 317	1396	1467, 1510, 1573, 1618	–	–	3087	3250–3600
Poly-2,4,6-TCP (CV) (Fig. 4(b))	858	761, 820	1004	1140–1250	–	1450–1600	1650–1800	2850–2960	–	–
Poly-2,4,6-TCP (0.78 V, 15 h) (Fig. 4(c))	858	757, 815	1002	1140–1250	1382	1440–1600	1640–1800	2850–2960	3019–3082	3400–3520
2,4,5-TCP (Fig. 4(a))	678, 730, 871 [25]	–	1072	1130–1300	1394	1457, 1481 1564, 1595	–	–	3028–3092	3450–3510
Poly-2,4,5-TCP (CV) (Fig. 4(b))	681, 877	761	1081	1080–1300	1351	1450–1600	1640–1800	2850–2960	3091	3440–3520
Poly-2,4,5-TCP (0.78 V, 15 h) (Fig. 4(c))	681, 878	759	1081	1120–1300	1351	1450–1600	1640–1800	2850–2960	3091	~3510
2,3,6-TCP (Fig. 4(a))	798 [25]	–	1102	1110–1300	1328	1407, 1466, 1567	–	–	3089	3200–3500
Poly-2,3,6-TCP (CV) (Fig. 4(b))	–	759, 815	1054	1120–1300	1377, 1395	1410–1600	1640–1800	2850–2960	3075	–
Poly-2,3,6-TCP (0.78 V, 15 h) (Fig. 4(c))	–	759, 811	1054	1120–1300	1378, 1396	1438, 1583	1650–1800	2850–2960	3077	~3520
PCP (Fig. 4(a))	707, 770 ($B_{\text{-C=C-}}$)	–	985	1194, 1219, 1305	–	1382, 1418, 1546	–	–	–	3250–3550
Poly-PCP (CV) (Fig. 4(b))	716, 803 ($B_{\text{-C=C-}}$)	758	9851	1150–1280	–	1380–1550	1650–1810	2850–2960	–	3250–3550
Poly-PCP (0.78 V, 15 h) (Fig. 4(c))	714 ($B_{\text{-C=C-}}$)	760	950	1150–1280	~1365	1380–1580	1650–1810	2850–2960	–	–

*Except pentachlorophenol monomer; † C—H (sp^3 hybridization) bending of the $-CH_2$ ir $-CH_3$ groups at 1450–1465 cm^{-1}) [24], in the case of the polymers formed which have deeper oxidized products (with cleavage benzene or quinone ring) in their mixtures may be present.

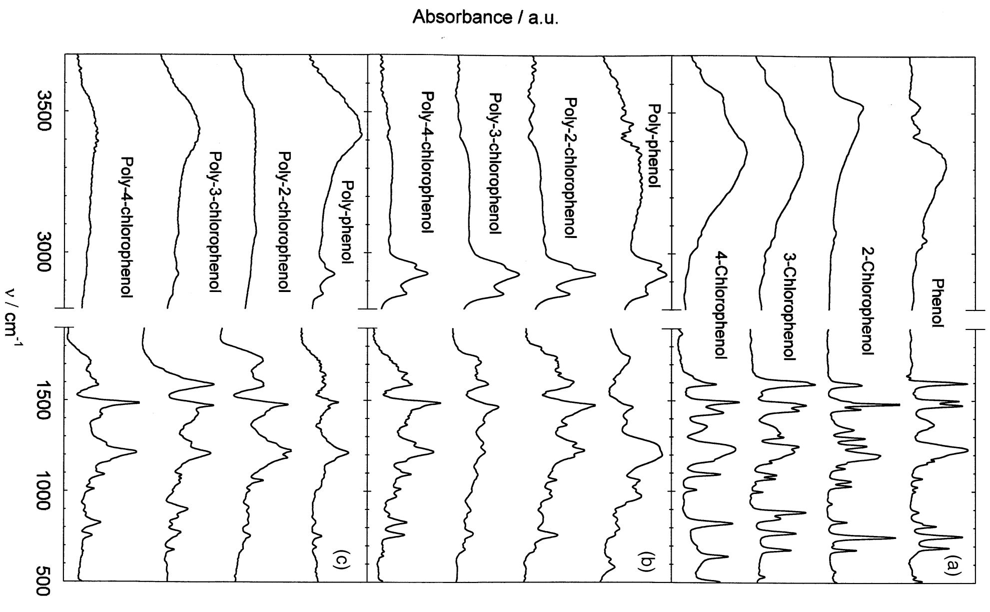

Fig. 1. FTIR spectra of phenol, 2-chlorophenol, 3-chlorophenol, 4-chlorophenol monomers (a) and the polymers (b, c), deposited on Pt net-sheet electrode under CV conditions (from −0.8 to 0.85 V vs (SHE) (b) and during potentiostatic electrolysis (0.78 V vs SHE, 15 h) (c).

the formation of corresponding diols and their further oxidation to quinone-type compounds. Several ill-defined bands at 1450–1600 cm^{-1} (Tables 1–3) in the IR spectra of the polymers (Figures 1(b,c)–4(b,c)) confirm the aromatic nature of the high molecular weight substances formed.

The bands at 2855, 2925 and 2958 cm^{-1} are due to sp^3 hybridized carbon C—H stretching vibrations [23, 24]. However, these bands in the polymers derived from the phenolic compounds (phenol [2, 4] and *o,o′*-biphenol [2]) during electropolymerization are associated with the quinone-type C—H stretching [2] or with analogous vibrations of multisubstituted benzene [4]. The presence of these vibrations in the IR spectra of most of the polymers formed could be explained by the cleavage of the benzene or quinone ring and further addition of $OH^{\bullet}$ and $HO_2^{\bullet}$ species to the cleaved structures. These radicals could be generated on the electrode surface reaching the potential of significant oxygen evolution (0.85 V vs SHE). This assumption is confirmed by the comparison of the IR spectra for the polymers formed under

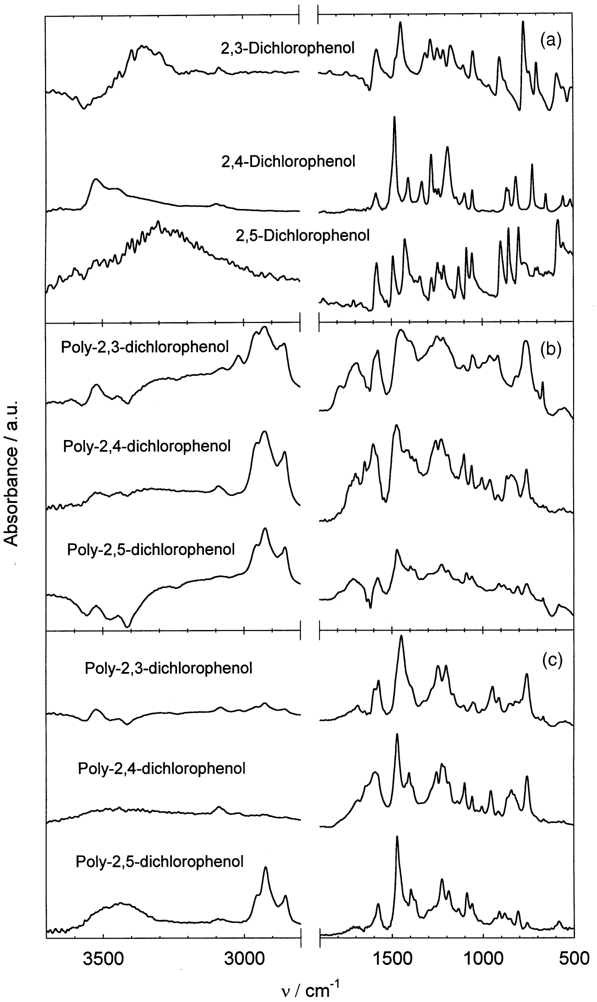

Fig. 2. FTIR spectra of 2,3-dichlorophenol, 2,4-dichlorophenol, 2,5-dichlorophenol monomers (a) and the polymers (b, c), deposited on Pt net-sheet electrode under CV conditions (from −0.8 to 0.85 V vs SHE) (b) and during potentiostatic electrolysis (0.78 V vs SHE, 15 h) (c).

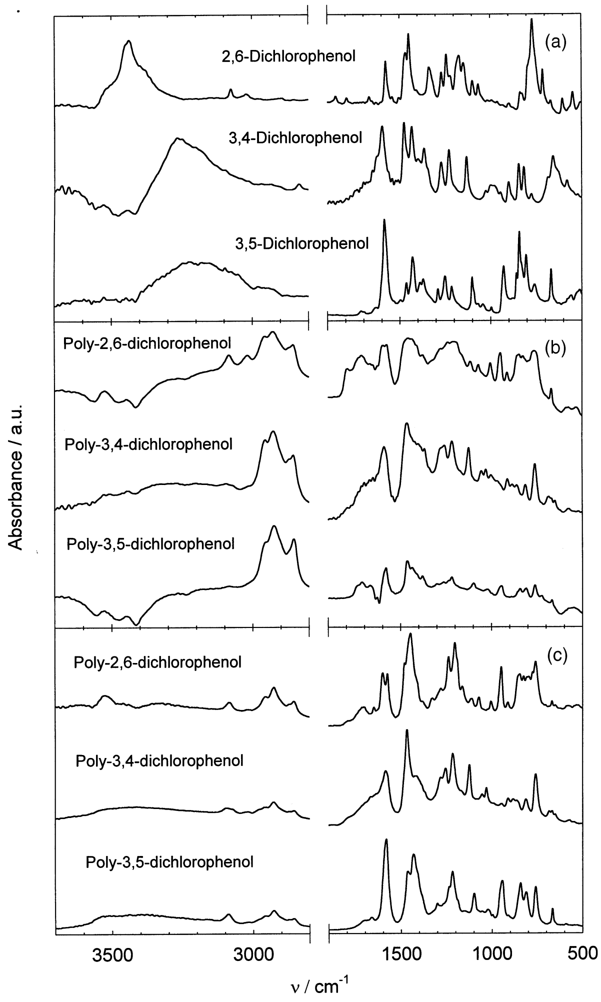

Fig. 3. FTIR spectra of 2,6-dichlorophenol, 3,4-dichlorophenol, 3,5-dichlorophenol monomers (a) and the polymers (b, c), deposited on Pt net-sheet electrode under CV conditions (from −0.8 to 0.85 V vs SHE) (b) and during potentiostatic electrolysis (0.78 V vs SHE, 15 h) (c).

potentiostatic (Figures 1(c)–4(c)) and potentiodynamic conditions (Figures 1(b)–4(b)). The intensities of the bands at 2850–2960 cm^{-1} in the IR spectra for the polymers formed under potentiodynamic conditions are more intense compared to those for the potentiostatically deposited high molecular weight substances. These differences can be explained by the higher concentration of oxidants ($OH^{\bullet}$ and $HO_2^{\bullet}$) at the electrode surface under potentiodynamic conditions when reaching oxygen evolution (0.85 V vs SHE) compared to the potentiostatic electrolysis at 0.78 V vs SHE. Vibrations in the range 3200–3600 cm^{-1} (Tables 1–3) in the IR spectra for most of the polymers correspond to weak O—H group stretching. The intensities of hydroxyl groups in the polymers (Figures 1(b,c)–4(b,c)) are rather less intense than those in the corresponding monomers (Figures 1(a)–4(a)) or are totally absent. This may be explained by the formation of high molecular weight substances through polymerization *via* the hydroxyl group and consequent formation of ether, diol and quinone structures. As a result polymeric species are formed with much more benzene rings per hydroxyl group (compared to the corresponding monomer, containing one hydroxyl group per benzene unit).

Vibrations of mild intensities at 1000–1100 cm^{-1} in the IR spectra of chlorinated phenol monomers correspond to C—Cl stretching (Figures 1(a)–4(a)) [25]. The wavelength number of these one or two sharp bands varies depending on the chlorination degree and the isomerism of each chlorinated phenol [25]. These vibrations may also be expected in the IR spectra of the corresponding polymer (Figures 1(b,c)–4(b,c)) by analogy to the monomer spectra. However, this frequency region (1000–1100 cm^{-1}) is characteristic for the 'fingerprints' of each individual compound and is rarely used for a common qualitative analysis. Moreover, the bands at 1000–1100 cm^{-1} are even less intense due to the slope of the baseline in the IR spectra for most of the polymers (Figures 1(b,c)–4(b,c)). The presence of C—Cl bonds in the IR spectra could be additionally confirmed by the shift of the carbonyl group vibrations to 1800 cm^{-1} (due to the negative inductive effect of chlorine atoms) (Figures 1(b,c)–4(b,c)). Such a shift is not characteristic for the IR spectra of polyphenol

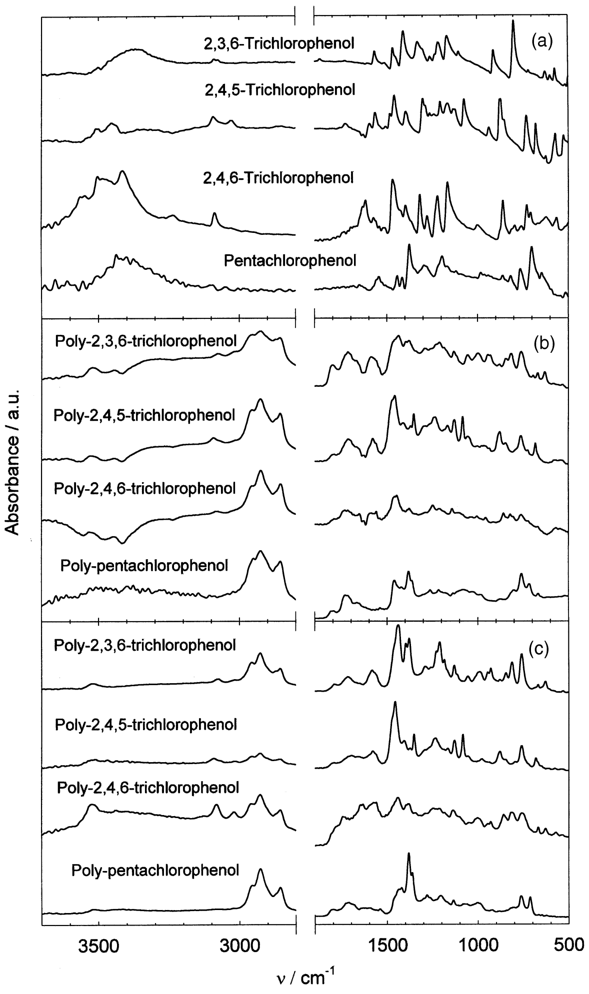

Fig. 4. FTIR spectra of 2,3,6-trichlorophenol, 2,4,5-trichlorophenol, 2,4,6-trichlorophenol, pentachlorophenol monomers (a) and the polymers (b, c), deposited on Pt net-sheet electrode under CV conditions (from −0.8 to 0.85 V vs SHE) (b) and during potentiostatic electrolysis (0.78 V vs SHE, 15 h) (c).

(Figure 1(b,c)). Therefore, it may be concluded that the cleavage of the C—Cl bond during the electropolymerization of chlorinated phenols occurs only to some extent or not at all.

The FTIR analyses of the polymeric substances formed from phenol and chlorinated phenols: monochlorophenols, dichlorophenols, 2,3,6-, 2,4,5-, 2,4,6-trichlorophenols and pentachlorophenol on the surface of Pt electrode under potentiostatic conditions prior to significant oxygen evolution (0.78 V vs SHE) and under CV conditions (−0.8 to 0.85 V) show common features (Tables 1–3 and Figures 1–4), which can be summarized as follows:

(i) The polymeric species formed have aromatic nature and are of ether–quinone origin. The presence of the ether links is confirmed by the stretching vibrations (1100 to 1300 cm^{-1}) of the =C—O—C= group in combination with the absence of vibrations corresponding to O—H stretch (3200–3700 cm^{-1}) in most cases. The presence of the carbonyl group (C=O) is confirmed by the stretching vibrations at (1630 to 1800 cm^{-1}). Out-of-plane vibrations of =C—H structures at 760 cm^{-1}, which are not characteristic of the IR spectra of corresponding monomers, indicate that during the electropolymerization of phenols quinone-type structures are formed. The aromatic nature of the polymers is evident from the stretching vibrations at 1450 to 1600 cm^{-1} (3–4 bands). Vibrations at 3200 to 3600 cm^{-1} in the IR spectra for most of the polymers correspond to a weak O—H group stretching. The hydroxyl group bands in the polymers are rather less intense compared to those in the corresponding monomers, suggesting a moderate degree of polymerization during electrooxidation of the phenols studied.

(ii) Vibrations at 2850–2960 cm^{-1}, which are present in most of the IR spectra of the polymers formed, correspond to stretching vibrations of the sp^3 hybridized carbon C—H bond. These vibrations are absent in the IR spectra of the monomers. The appearance of these bands indicates that during the electrooxidation–electropolymerization of phenol and its chlorinated derivatives a cleavage of the benzene ring (most probably the cleavage of the quinone ring) occurs to some extent. The corresponding structures presumably participate in further addition/elimination reactions with such oxidants as hydroxyl radicals (OH$^\bullet$) or peroxyl radicals ($HO_2^\bullet$) generated on the electrode surface at potentials of oxygen evolution. The intensities of these bands in the case of the CV-deposited polymers are greater compared to the IR spectra of the polymers obtained under potentiostatic oxidation conditions. Significant oxygen evolution starts at the electrode potential more positive 0.85 V vs SHE and, therefore, the concentration of corresponding radical species is greater compared to potentiostatic electrolysis (0.78 V vs SHE). These bands are absent in the oxidation–polymerization products for monochlorophenols under potentiostatic conditions; slight intensities are visible in the case of dichlorophenols and the most intense ones in the polymerization products of trichlorophenols (except 2,4,5-trichlorophenol) and pentachlorophenol. The presence of the sp^3 C—H vibrations in the case of oxidation of pentachlorophenol polymerization products confirms that the electrochemically generated oxidants participate in the formation of such deeper oxidized species [27].

(iii) The shift of the C=O group stretching vibrations from 1630 to 1800 cm^{-1}, which is mostly characteristic of the polymeric products of trichlorophenols and pentachlorophenol, indicates that chlorine atoms are present in the polymeric structures and are distinctive due to the negative inductive effect (−I). The C—Cl bond stretching vibrations at 1050–1100 cm^{-1} for most of the polymers also confirm the presence of chlorine atoms. This suggests that only a partial dechlorination, if any, occurs during the electropolymerization of chlorophenols. Evaluation of the degree of dechlorination of chlorophenols during their electropolymerization, as studied using gas chromatography mass spectrometry, will be presented elsewhere [26]. The GC–MS data [26] give direct evidence of the partial chlorine loss from the active *ortho* and *para* positions, while no dechlorination occurs from the *meta* position during electropolymerization/oligomerization of the chlorophenols. Similar conclusions were made based on the mass-to-charge ratio for potentiostatic electropolymerization of chlorophenols studied by EQCM [19].

5. Conclusions

(i) The IR spectra of the polymers formed during electropolymerization of phenol and chlorinated phenols confirm the aromatic nature of the high molecular weight substances. This suggests that a coupling of monomers occurs during the electrooxidation of the phenolic compounds.

(ii) The presence of vibrations characteristic of ether linkages and the absence of vibrations of hydroxyl groups in the IR spectra of the polymers formed suggest that the coupling of the monomers occurs through the formation of the $=C-O-C=$ links.

(iii) Vibrations in the IR spectra of the polymers characteristic of quinone and more saturated species reveal a deeper oxidation of the high molecular weight substances formed. This effect is most pronounced at more positive potentials, when significant oxygen evolution starts.

(iv) The characteristic vibrations for C—Cl bonds and the shift of the carbonyl group vibrations due to the negative inductive effect of chlorine atoms in the IR spectra of the polymers formed imply that only partial chlorine elimination, if any, occurs during the electropolymerization of chlorophenols.

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