



Electropolymerization of chlorinated phenols on a Pt electrode in alkaline solution. Part IV: A gas chromatography mass spectrometry study

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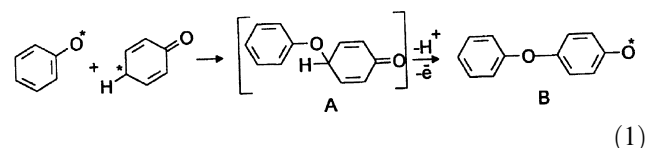
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Abstract

The electropolymerization of phenol and chlorinated phenols (monochlorophenols, dichlorophenols, 2,3,6-, 2,4,6-, 2,4,5-trichlorophenols and pentachlorophenol) was studied on a platinum electrode at 0.78 V vs SHE in alkaline 1 M NaOH aqueous solutions containing 0.1 M of the phenols. The low molecular weight reaction products were investigated by means of gas chromatography mass spectrometry (GCMS). Product analyses show that oligomers (dimers, trimers and tetramers) are present in the polymer mixtures formed. The MS spectra reveal the ether-linked nature of the oligomers formed during the electrooxidation-electropolymerization of the phenolic compounds. The mass spectra of the low molecular weight substances formed suggest that the oxidation-polymerization of phenols proceeds following two different mechanisms: (i) through the quinol-ether route (without chlorine elimination) and (ii) via the nucleophilic-radical substitution ($S_{RN}1$) route (with some elimination of chlorine from *ortho* and/or *para* positions).

1. Introduction

The electrooxidation of most phenolic compounds proceeds following two subsequent steps: the formation of the radicals from phenoxide anions and further anion-radical or radical-radical coupling with the formation of oligomers and polymers. The coupling proceeds through formation of an unstable intermediate quinol-ether (A) [1–4], with further elimination of a proton, an oxidation step and the formation of a dimer-radical (B):



A total electropolymerization reaction following this route of the polymeric compound formation is a two-electron process per monomer molecule. The oxidation of radicals to form the corresponding cations is less likely because the potentials of oxidation of the phenoxide anions to radicals are rather low, compared with those of oxidation of the radicals to cations [5].

The nature of the electropolymerization products of phenols strongly depends on the reaction medium. In alkaline solutions the formation of the C–O–C bonds prevails over the C–C coupling, while in acidic solutions the carbon–carbon coupling is more favoured compared to formation of the ether linkages [6, 7].

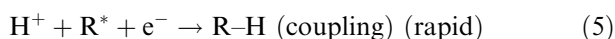
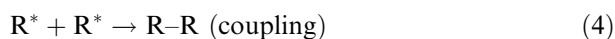
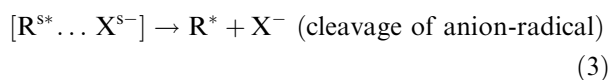
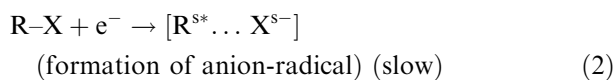
Investigations of anodic oxidation of various phenolic compounds, which have at least one substituent-free *ortho* or *para* position, show that the electropolymerization leads to the formation of *ortho* and/or *para* substituted derivatives [5, 8–14]. This is in accordance with stabilization of the radicals formed due to a positive mesomeric effect (M^+) of the phenoxide oxygen.

For the phenolic compounds with all *ortho* and *para* positions occupied by atoms or groups other than hydrogen, a coupling occurs through different routes. For example, in the case of oxidation of 2,4,6-trimethylphenol (TMP) the corresponding radical formed initially is unstable and its isomerization may lead to the hydroxybenzyl radical or to the loss of a hydrogen atom resulting in a quinone-methide intermediate [13, 15]. McNellis reported that oxidation of TMP by MnO_2 yields an oligomer of poly(dimethylphenylene oxide) as a consequence of the methyl group cleavage [13, 16]. Using potassium nitrodisulfonate as an oxidizing agent Magnusson obtained dimethylquinone, 4-hydroxybenzyl alcohol and benzylphenyl ether as oxidation products [13, 15].

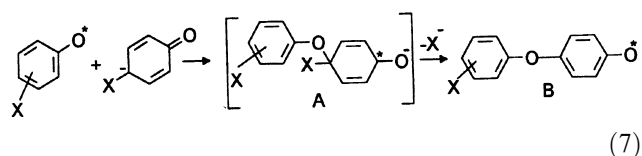
The anodic oxidation of phenols bearing halogen substituents proceeds with some halogenide elimination in addition to the carbon–oxygen coupling mechanism mentioned above. This phenomenon was even more pronounced for the oxidation of 2,6-dimethyl-4-bromophenol [4]. The C–X bond (where X is a halogen atom) cleavage observed during electropolymerization of 2-bromophenol and 2,6-dimethylphenol-4-bromophenol

also has an analogue in a chemical polymerization [4, 17]. In the case of the latter compound the coulombic yield shows the stoichiometry of monomer polymerization well above a standard value of 0.5 mol F⁻¹ indicative of the occurrence of polymerization through the chain-reaction. In the case of copolymerization of 2-bromophenol with allylamine the polymeric compounds with about 30% loss of the bromine are formed [4]. An analogous polymerization reaction occurs in the case of 2,6-dichlorophenol [4] and pentachlorophenol (PCP) oxidation [5]. A 19% loss of chlorine in the case of 2,6-dichlorophenol polymerization was found [4]. In the case of PCP electropolymerization the reaction products depend on the electrode potential applied [5] ranging from the onset of PCP oxidation to the onset of oxygen evolution. Over a wide potential range the PCP electro-oxidation was found to be one-electron reaction resulting in 2,3,4,5,6-pentachloro-4-pentachlorophenoxy-2,5-cyclohexadienone [5]. At very low overpotentials the reaction products became more complex with formation of chloride and neutral radical (of a higher molecular weight) and thus continuing the electropolymerization reaction [5].

In general, elimination of the halogen during oxidation of halophenols proceeds following a radical-nucleophilic mechanism S_{RN}1 [18, 19]. Reduction of most halogenated organic compounds follows this mechanism as can be expressed by the equations [20]:



Formation of anion-radicals during the oxidation-polymerization of halogenated phenolic compounds is analogous to the reduction process of halogenated organic species but differs in the manner of anion radical formation. During oxidation the anion-radical is formed following the reaction between the phenoxide anion and the corresponding radical:



The rate of the C-X bond cleavage in the intermediate anion-radical formed (A) depends considerably on the energy of the bond. Therefore, the reactivity of halogenated organic species decreases in the order:

I > Br > Cl ≫ F [19]. The dimer-radical (B) formed after the cleavage of halogenide anion is involved in further coupling/polymerization.

Due to a large variety of electropolymerization products depending on the monomer structure, applied potential and the solution pH, characterization of the products formed under defined experimental conditions is necessary to better understand the electropolymerization routes of chlorophenols. In previous papers we reported data on the electropolymerization of chlorophenols studied by CV [21], EQCM [22] and FTIR [23]. In the present work the electropolymerization was carried out on a Pt electrode at a constant anodic potential prior to oxygen evolution in 1 M NaOH solution containing 0.1 M of corresponding chlorophenols under the same experimental conditions as these applied for the EQCM [22] and FTIR [23] studies. The reaction products were characterized by the GCMS analysis of chloroformic solutions of the electropolymerization mixtures. The electropolymerization routes for the monomers of a different composition and structure are discussed on the basis of the GCMS data.

2. Experimental details

A potentiostat PI-50-1 and a function generator PR-8 were used to conduct the electrolysis in a potentiostatic mode. The electrochemical measurements were carried out using a working Vinkler (Pt net-sheet) electrode (6 cm × 6 cm, real surface area 1736 cm²) at 0.78 V vs SHE for 15 h. The real surface area of the working electrode was determined from the hydrogen monolayer adsorption charge [24, 25] in 0.5 M sulfuric acid solution. A Pt foil counter electrode (1 cm × 1 cm) and an Ag/AgCl/KCl_(sat.) reference electrodes were used. A three-electrode cell of working volume of 60 ml was used for the electrochemical measurements. Analytical grade chemicals (Fluka, Aldrich, Riedel-de-Häen) and triply distilled water were used to prepare the solutions. All the solutions were purged by an argon stream to remove oxygen during electrochemical experiments.

The GCMS measurements were carried out using a Star 3400 C_x gas chromatograph, equipped with the 'ion trap' type mass selective detector Saturn 3 (Varian, USA). The electron impact mode (70 eV), enabling sufficient fragmentation of the molecular ions, was used for ionization of the molecules. The mass range selected for monitoring was 45 to 650 *m/z*. The temperature of the ion source was 200 °C. A capillary column DB-5 (30 m, i.d. × 0.25 mm) (J&W, USA) was used for a chromatographic separation of the components of the polymerization mixtures. For the separation of the components the following column temperature program was used: 60 to 300 °C (7 °C min⁻¹) and after that holding for 35 min at 300 °C. For the qualitative GC-MS analyses an aliquot of the chloroformic solution of

electropolymerization products (5 μ l) was introduced into the gas chromatograph using a split/splitless 1077 injector in the splitless mode at 300 °C. The absence of the oxidation products in all the original chemicals used for experiments was checked by the GCMS.

3. Results

The GCMS analyses of the polymers formed during the electrooxidation–electropolymerization of phenol and its chlorinated derivatives show that the low molecular weight oligomers (dimers, trimers and tetramers) are incorporated in the polymeric mixtures (Figures 1–5). The GCMS detection of higher oligomers is complicated due to a detection limit of the mass analyzer used (up to $m/z = 650$) and a low mobility of the high molecular weight species in the capillary column of the chromatograph. However, despite these limitations, the electropolymerization pathways can be distinguished from the GCMS analysis of the oligomers formed assuming that the same coupling mechanism is valid for both oligomeric and polymeric species formation.

The mass spectra of phenol electropolymerization products were compared with those in the computer mass spectra library (NIST 92) and revealed that mainly ether-linked oligomers are formed (Figure 1) in accordance with literature data, suggesting that the C–O–C links prevail over the C–C links for the electropolymer-

ization in alkaline medium [5, 7, 23]. *Para(ortho)*-substituted dimer (Figure 1(a)), trimer (Figure 1(b)) and tetramer (Figure 1(c)) were identified (linking through *meta*-position is less favourable [26]).

In the case of the electropolymerization of all monochlorophenols (MCPs) the corresponding dimers ($M^{+\bullet}$ of $m/z = 220 + 222$ with 1 Cl atom; $254 + 256 + 258$ with 2 Cl atoms) (Figure 2(a) and (b)) and trimers ($M^{+\bullet}$ of $m/z = 346 + 348 + 350$ with 2 Cl atoms; $380 + 382 + 384$ with 3 Cl atoms) (Figure 2(c) and (d)) are formed through the C–O–C linking of monomers. The presence of the dimers and trimers with $M^{+\bullet}$ of $m/z = 254 + 256 + 258$ (Figure 2(b)) and $m/z = 380 + 382 + 384$ (Figure 2(d)) indicates that the electropolymerization occurs through the ether-quinol route (Equation 1).

The presence of dimers and trimers ($M^{+\bullet}$ of $m/z = 220 + 222$ with 1 Cl atom and $m/z = 346 + 348 + 350$ with 2 Cl atoms) (Figure 2(a) and (c)) in the electropolymerization mixtures of 2-monochlorophenol (2-MCP) and 4-monochlorophenol (4-MCP) suggests that the elimination of chlorine occurs to some extent via a nucleophilic-radical substitution ($S_{RN}1$) mechanism (Equation 6).

The GCMS analysis of the electropolymerization products of 3-monochlorophenol (3-MCP) (Figure 2(b) and (d)) shows only dimers and trimers formed according to Equation 1. This implies that chlorine elimination does not occur from the *meta* position, while *ortho* and

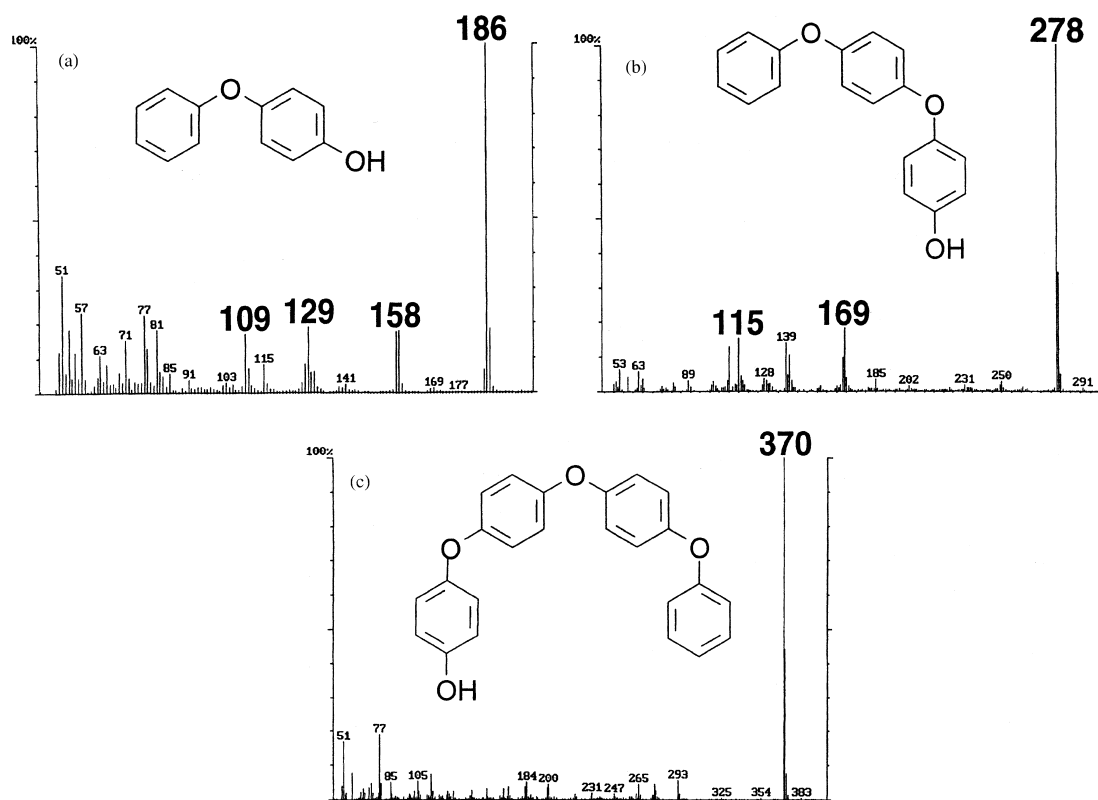


Fig. 1. Mass spectra and possible structures of dimeric (a), trimeric (b) and tetrameric (c) phenol electropolymerization products. Electropolymerization was carried out on a Pt electrode at 0.78 V (SHE) in 1 M NaOH containing 0.1 M of phenol; time 15 h, temperature 20 °C.

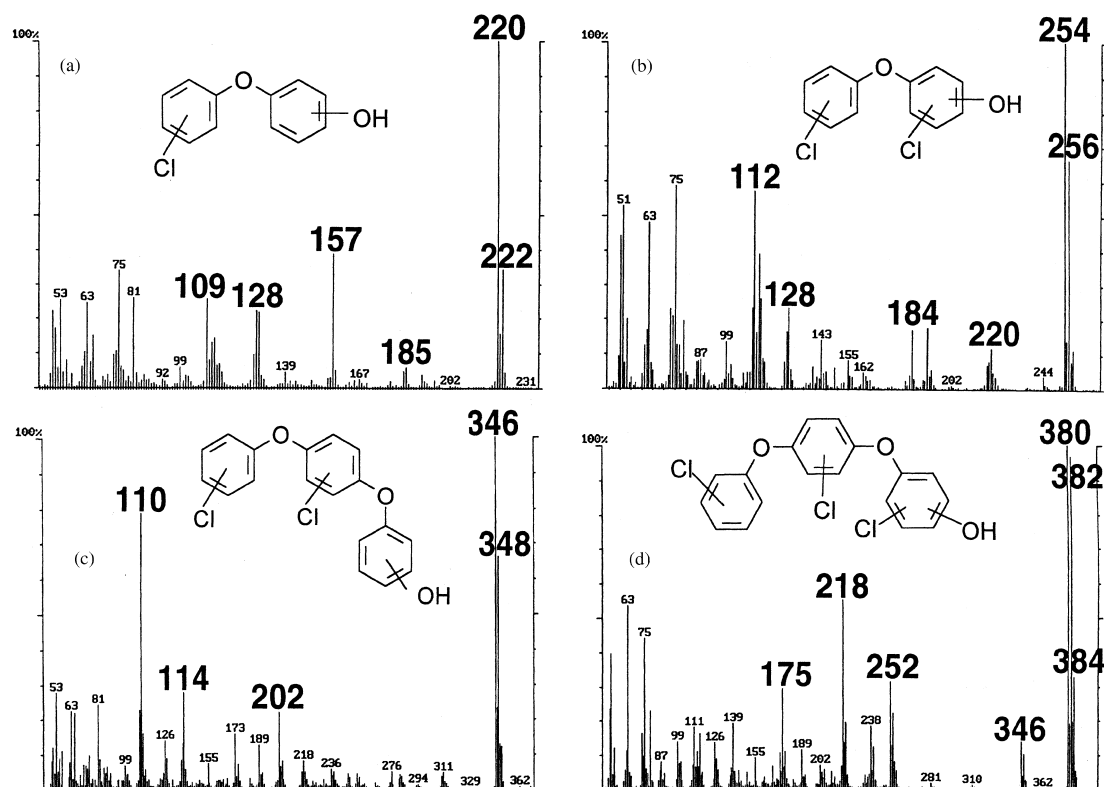


Fig. 2. Mass spectra and possible structures of dimeric (a, b), trimeric (c, d) products obtained during the electropolymerization of monochlorophenols according to $S_{RN}1$ (a, c) and quinol-ether (b, d) mechanisms. Electropolymerization conditions are the same as in Figure 1.

para positions are active. This is in accordance with distribution of the electron density in the corresponding anions and radicals which are stabilized through a delocalization of the electron density at *ortho* and *para* but not *meta* positions [26]. From the latter it follows that the oligomers formed are most likely *ortho* and *para* substituted derivatives. However, a differentiation between the positional oligomeric isomers by means of GC-MS is rather complicated due to very similar (nearly identical) mass spectra of these compounds.

The electro polymerization mixtures of dichlorophenols (DCPs) also contain mainly dimers ($M^{+\bullet}$ of $m/z = 288 + 290 + 292$ with 3 Cl atoms; $m/z = 322 + 324 + 326$ with 4 Cl atoms) (Figure 3(a) and (b)) and trimers ($M^{+\bullet}$ of $m/z = 414 + 416 + 418$; $448 + 450 + 452$; $482 + 484 + 486$) (Figure 3(c)–(e)) which, most likely, are ether-linked and *ortho*-, *para*-substituted species. Dimers ($M^{+\bullet}$ of $m/z = 322 + 324 + 326$ with 4 Cl atoms) (Figure 3(b)) and trimers ($M^{+\bullet}$ of $m/z = 482 + 484 + 486$ with 6 Cl atoms) (Figure 3(e)) are formed through the quinol-ether mechanism (Equation 1) while other oligomers (Figure 3(c) and (d)) are the products of the electropolymerization through the $S_{RN}1$ mechanism (Equation 6). The GCMS analysis of the electropolymerization products of 3,5-dichlorophenol (3,5-DCP) shows no dimers and trimers with eliminated chlorine atoms. This strongly suggests that the electropolymerization of this isomer occurs thoroughly through the quinol-ether mechanism (Equation 1) as in the case of 3-monochlorophenol oxidation. This confirms an assump-

tion that the electropolymerization of phenolic compounds occurs through the active *ortho* and *para* positions rather than *meta* position and is in agreement with the literature data [14].

The electro polymerization mixtures of 2,4,5-trichlorophenol (2,4,5-TCP) and 2,3,6-trichlorophenol (2,3,6-TCP) contain dimers ($M^{+\bullet}$ of $m/z = 356 + 358 + 360$ with 5 Cl atoms; $m/z = 390 + 392 + 394$ with 6 Cl atoms) (Figure 4(a) and (b)) and trimers ($M^{+\bullet}$ of $m/z = 516 + 518 + 520$ with 7 Cl atoms; $m/z = 550 + 552 + 554$ with 8 Cl atoms; $m/z = 584 + 586 + 588$ with 9 Cl atoms) (Figure 4(c)–(e)). The presence of these compounds in the electropolymerization mixture suggests that electrooxidation proceeds through both quinol-ether and $S_{RN}1$ mechanisms.

The electro polymerization mixture of 2,4,6-trichlorophenol (2,4,6-TCP) contains dechlorinated dimers ($M^{+\bullet}$ of $m/z = 356 + 358 + 360$ with 5 Cl atoms) (Figure 4(a)) and trimers with $M^{+\bullet}$ of $m/z = 516 + 518 + 520$ with 7 Cl atoms (Figure 4(c)) and $M^{+\bullet}$ of $m/z = 550 + 552 + 554$ with 8 Cl atoms (Figure 4(d)). However, fully-chlorinated dimers ($M^{+\bullet}$ of $m/z = 390 + 392 + 394$) and trimers ($m/z = 584 + 586 + 588$) are absent. This implies that the electropolymerization of this isomer proceeds exclusively via the $S_{RN}1$ mechanism. The nonachloro-2-phenol and nonachloro-4-phenol species, identified in the electropolymerization mixture of pentachlorophenol, also indicate that the coupling occurs thoroughly via the $S_{RN}1$ mechanism (Figure 5(a) and (b)).

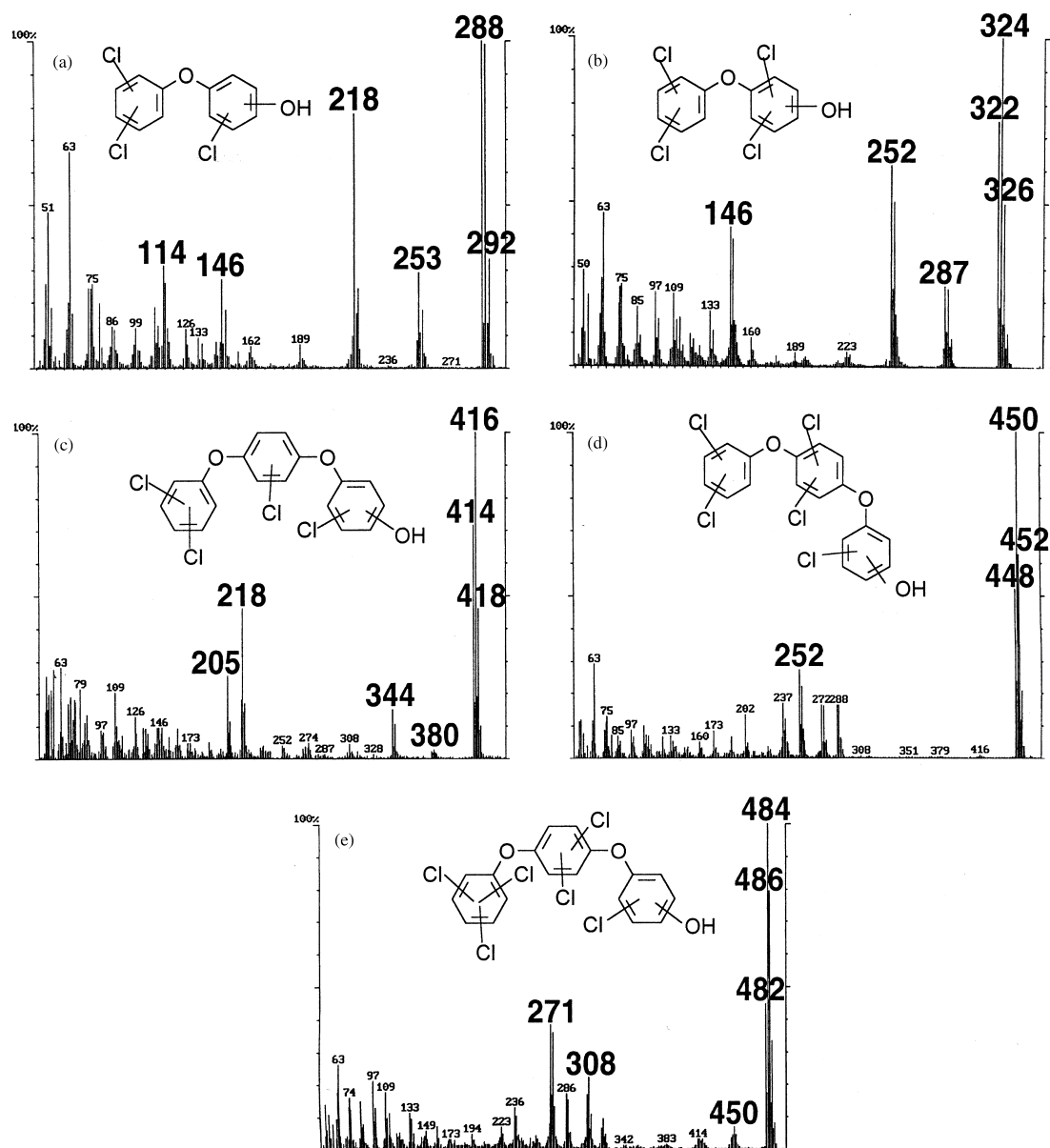


Fig. 3. Mass spectra and possible structures of dimeric (a, b) and trimeric (c, d, e) products obtained during the electropolymerization of dichlorophenols according to $S_{RN}1$ (a, c, d) and quinol-ether (b, e) mechanisms. Electropolymerization conditions are the same as in Figure 1.

4. Discussion

The GCMS analysis of the oligomeric species formed in the course of electropolymerization of chlorophenols gives direct evidence of dechlorination of some monomers as a result of electropolymerization and allows to distinguish between the ether-quinol (without Cl elimination) and $S_{RN}1$ (with Cl elimination) reaction routes, assuming that the same coupling mechanism is valid for both oligomeric and polymeric species formation and no additional dechlorination occurs during separation/injection procedures.

For the semiquantitative evaluation of the total dechlorination degree during the electropolymerization of chlorophenols the ratio of dechlorinated and fully chlorinated oligomers has been calculated from the corresponding mass spectra. A semiquantitative evalu-

ation of the total chlorine elimination during the electropolymerization of chlorophenols shows (Table 1) that both 2,4,6-trichlorophenol and pentachlorophenol monomers (all *ortho* and *para* positions substituted by chlorine atoms) are coupled exclusively through the $S_{RN}1$ mechanism. A monomer coupling through the $S_{RN}1$ mechanism is most pronounced also for both *ortho* and *para* Cl-substituted monomers (2,4-DCP and 2,4,5-TCP), while it is less pronounced for either *ortho*-(2-MCP; 2,3-MCP; 2,5-MCP; 2,6-MCP and 2,3,6-TCP) or *para*-substituted chlorophenols (4-MCP and 3,4-MCP). The GC-MS data of Table 1 are in a fair agreement with the conclusions concerning the electropolymerization routes of chlorophenols derived on the basis of the EQCM data [22].

However, it should be noted, that the initial phenoxy radical involved in coupling through the $S_{RN}1$ route

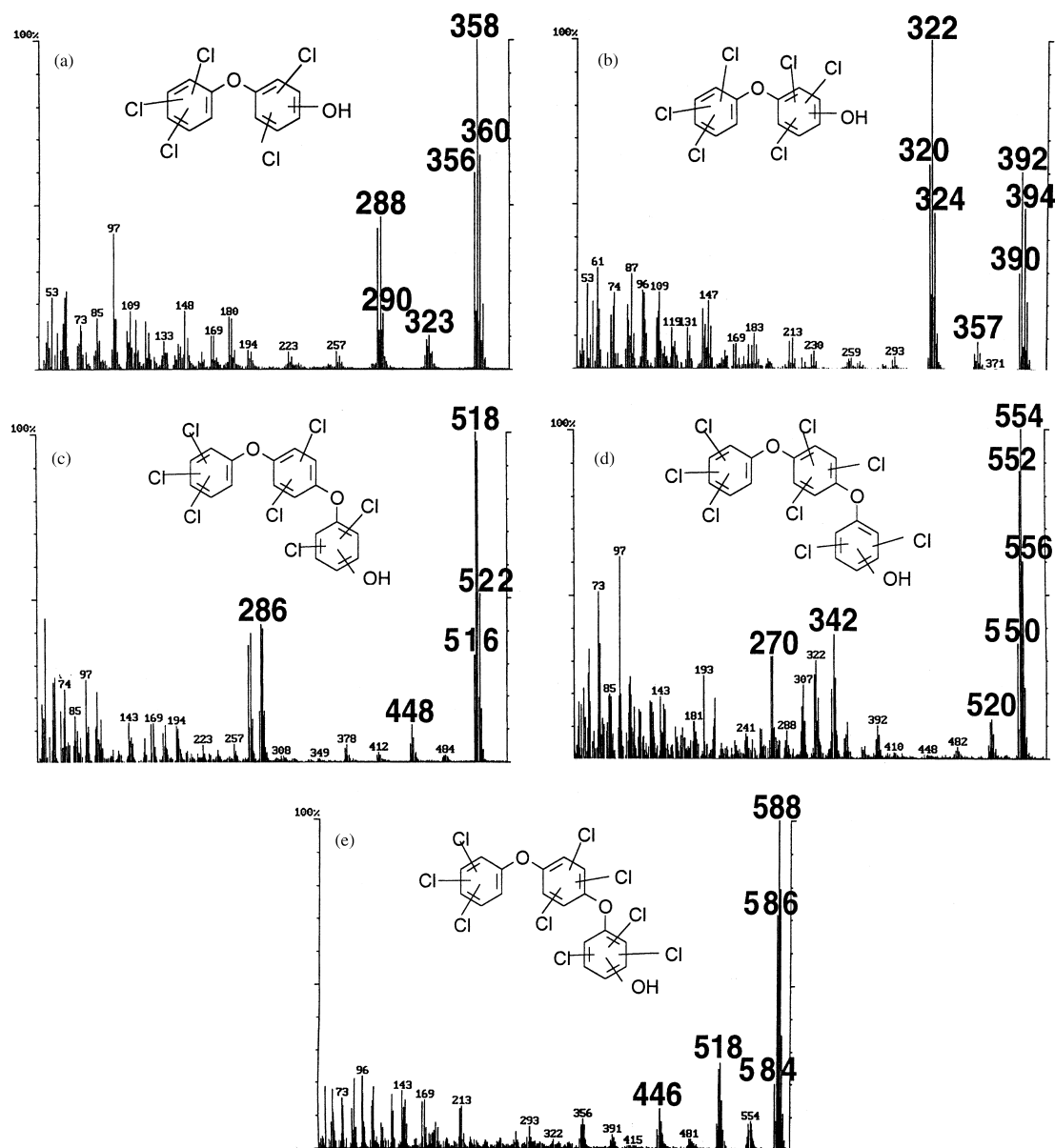


Fig. 4. Mass spectra and possible structures of dimeric (a, b) and trimeric (c, d, e) products obtained during the electropolymerization of trichlorophenol according to $S_{RN}1$ (a, c, d) and quinol-ether (b, e) mechanisms. Electropolymerization conditions are the same as in Figure 1.

(Reaction 6) is not dechlorinated at all (not taking into account a hardly possible 'head-to-tail' close-loop formation of the growing oligomer). Therefore, an actual dechlorination degree for the MCP dimers can be assumed 50% (1 Cl loss of total 2 Cl) or 100% (1 Cl loss of 1 Cl available). A small total amount of dechlorinated MCP dimers (Table 1, 2% for 2-MCP and 5% for 4-MCP) is due to the accessibility of alternative Cl-free *ortho* and *para* positions (only one of three active *ortho* and *para* positions is occupied by the Cl-substituent). This assumption is supported by the GCMS analysis of the MCP trimers, hardly any trimers with two eliminated Cl atoms are detected due to a low probability of further coupling through the same Cl-substituted position rather than via two alternative Cl-free active positions (Figure 2(c) and (d)). A dechlorination degree (if any) for the corresponding trimers is

33% (1 Cl substituted of total 3 Cl) or 50% (1 Cl eliminated of 2 Cl available), respectively. Correspondingly, no Cl-elimination occurs in 3-MCP dimers and trimers since all three Cl-unsubstituted active positions (2 *ortho* and 1 *para*) are available in this monomer.

An analogous evaluation of the dechlorination degree for the DCP dimers (Figure 3(a)) suggests that only 1 Cl can be eliminated of total 4 Cl (25%) or 1 Cl of 2 Cl available (50%). The probability of Cl elimination from the DCP monomers is higher for 2,4-DCP where one *ortho* and one *para* positions are Cl-substituted rather than two chlorinated *ortho* positions as in the case of 2,6-DCP (Table 1). This suggests that the *para* position is more active for the electropolymerization compared to *ortho* positions in agreement with the data for the MCP monomers (Table 1) and theoretical calculations [26]. In contrast, when two *meta* positions are Cl-

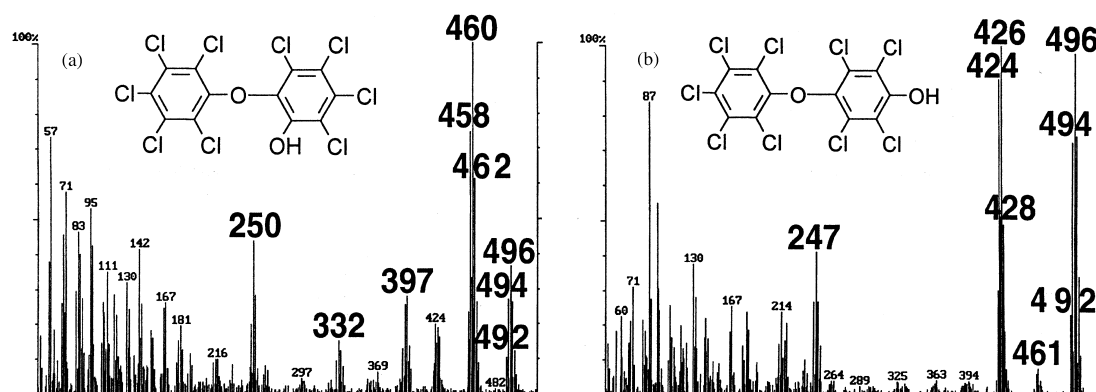


Fig. 5. Mass spectra of nonachloro-2-phenol (a) and nonachloro-4-phenol (b) obtained during the electropolymerization of pentachlorophenol according to $S_{RN}1$ mechanisms. Electropolymerization conditions are the same as in Figure 1.

Table 1. Semiquantitative evaluation of the total chlorine elimination from the oligomers formed during the electropolymerization of chlorophenols according to GCMS data

Electropolymerization was carried out on a Pt electrode at 0.78 V vs SHE for 15 h in 1 M NaOH solution containing 0.1 M of corresponding chlorophenol at 20 °C.

Monomer	$\sum m_{\text{dimers}}$ /%	$\sum m_{\text{dimers-Cl(s)}}$ /%	$\sum m_{\text{trimers}}$ /%	$\sum m_{\text{trimers-Cl(s)}}$ /%
2-MCP	98	2	93	7
3-MCP	100	–	100	–
4-MCP	95	5	86	14
2,5-DCP	95	5	86	14
2,4-DCP	74	26	38	62
2,3-DCP	94	6	91	9
2,6-DCP	99	1	89	11
3,4-DCP	98	2	93	7
3,5-DCP	100	–	100	–
2,3,6-TCP	98	2	88	12
2,4,5-TCP	62	38	75	25
2,4,6-TCP	–	100	–	100
PCP	–	100	–	100

substituted in the 3,5-DCP monomer, no Cl-elimination occurs (Table 1) and the electropolymerization proceeds entirely through the ether-quinol route (Reaction 1).

For the DCP trimers fully chlorinated species are also detected in the case of 3,5-DCP monomer electropolymerization (Figure 3(e)). The highest loss of 2 Cl atoms per trimer (Figure 3(c)) corresponds to the dechlorination degree of 33% (of total 6 Cl) or 50% (of 4 Cl available). The DCP trimer species of a lower dechlorination degree (Figure 3(d)) are also present in the electropolymerization mixture with 1 Cl loss of total 6 Cl (dechlorination about 17%) or of 5 Cl available (20% dechlorination).

Similar evaluation for the TCP isomers suggests that one (at least), two or all three active *ortho* and *para* positions can be Cl-substituted, depending on the Cl-substituent location. In the first two cases additional Cl-free active positions are available for the electropolymerization (either two or one Cl-substituent of total three chlorines are located in two inactive *meta* positions). Again, the *para* position demonstrates a higher

reactivity toward electropolymerization compared to *ortho* positions (Table 1, compare 2,3,6-TCP and 2,4,5-TCP). In the case of 2,4,6-TCP and PCP the electropolymerization occurs exclusively with Cl elimination ($S_{RN}1$ route, Reaction 6). The dechlorination degree for the TCP dimers varies from zero (Figure 4(b)) to approximately 17% (1 Cl loss of total 6 Cl) or 33% (1 Cl loss of 3 Cl available) (Figure 4(a)). Correspondingly, the TCP trimers can be fully chlorinated (Figure 4(e)) or partially dechlorinated by 22% of total chlorine or 33% of Cl available (Figure 4(c)), and 11% (1 Cl of total 9 Cl) or about 17% (1 Cl of 6 Cl available). Similarly, the dechlorination degree for the PCP dimers (Fig. 5) is 10% (1 Cl of 10 Cl total) or 20% (1 Cl of 5 Cl available).

5. Conclusions

The GCMS studies of phenol and its chlorinated derivative electropolymerization products show that the GCMS is a valuable method for evaluation of the oxidation–polymerization reaction mechanisms of these compounds. The GCMS analysis of the electropolymerization products of these phenolic compounds suggests that coupling of phenols occurs mainly through the C–O–C linkages.

The structure of the oligomers (dimers and trimers) formed reveals that the coupling of chlorinated phenols occurs through the active *ortho* and *para* positions following two different mechanisms: through the quinol-ether route (without chlorine elimination) or via the nucleophilic-radical substitution ($S_{RN}1$) mechanism with some elimination of chlorine if at least one *ortho* and/or *para* position are occupied by the Cl-substituent.

In the case of *meta*-substituted chlorinated phenols: 3-monochlorophenol and 3,5-dichlorophenol, the coupling occurs exclusively without elimination of chlorine while the electrooxidation-electropolymerization of 2,4,6-trichlorophenol and pentachlorophenol with all *ortho* and *para* positions occupied by chlorine atoms results in formation of the dimers and trimers with eliminated chlorine.

A semiquantitative evaluation of the amount of the dimers and trimers with the maximum number of chlorine atoms and those with eliminated from one to two chlorine atoms reveals that the most pronounced electropolymerization with elimination of chlorine occurs in the case of 4-monochlorophenol, 2,4-dichlorophenol and 2,4,5-trichlorophenol. A semiquantitative evaluation of the amounts of the dimers and trimers formed shows that *para*-substituted chlorophenols tend to couple following the $S_{RN}1$ mechanism rather than *ortho*-substituted isomers.

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References

- G.D. Cooper, H.S. Blanchard, G.F. Endres and H. Finkbeiner, *J. Am. Chem. Soc.* **87** (1965) 3996.
- G.D. Cooper and J.G. Bennet Jr, *J. Org. Chem.* **37** (1972) 441.
- M. Karhu, *J. Chem. Soc. Perkin Trans.* **1** (1981) 303.
- G. Mengoli, S. Daolio and M.M. Musiani, *J. Appl. Electrochem.* **10** (1980) 459.
- M. Gattrell and B. MacDougall, *J. Electrochem. Soc.* **146** (1999) 3335.
- P.I. Iotov and S.V. Kalcheva, *J. Electroanal. Chem.* **442** (1998) 19.
- G. Mengoli and M. Musiani, *J. Electrochem. Soc.* **134** (1987) 643C.
- M. Gattrell and D.W. Kirk, *J. Electrochem. Soc.* **140** (1993) 903.
- M. Gattrell and D.W. Kirk, *J. Electrochem. Soc.* **139** (1992) 2736.
- M. Gattrell and D.W. Kirk, *J. Electrochem. Soc.* **140** (1993) 1534.
- J. Wang, M. Jiang and F. Lu, *J. Electroanal. Chem.* **444** (1998) 127.
- F. Bruno, M.C. Pham and J.E. Dubois, *Electrochim. Acta* **22** (1977) 451.
- S.H. Glarum, J.H. Marshall, M.Y. Hellman and G.N. Taylor, *J. Electrochem. Soc.* **134** (1987) 81.
- S. Taj, M.F. Ahmed and S. Sankarapapavinasam, *J. Electroanal. Chem.* **356** (1993) 269.
- R. Magnusson, *Acta Chem. Scand.* **18** (1964) 759.
- E. McNelis, *J. Am. Chem. Soc.* **88** (1966) 1074.
- G.D. Staffin and C.C. Price, *J. Am. Chem. Soc.* **82** (1960) 3632.
- R.A. Rossi and R.H. Rossi, 'Aromatic substitution by the $S_{RN}1$ mechanism' (Russian edition, Moscow, 1986).
- I.P. Beleckaja and V.N. Drozd, *Uspekhi Khimii* **48** (1979) 793 (in Russian).
- M.M. Baizer, 'Organic Electrochemistry' (Marcel Dekker, New York, 1973).
- Z. Ežerskis and Z. Jusys, *J. Appl. Electrochem.* **31** (2001) 1117.
- Z. Ežerskis, G. Stalnionis and Z. Jusys, *J. Appl. Electrochem.*, **32** (2002) 49.
- Z. Ežerskis and Z. Jusys, *J. Appl. Electrochem.*, in press.
- W. Vielstich, 'Brennstoffelemente' (VCH, Weinheim 1965).
- H. Angerstein-Kozłowska, B.E. Conway and W.B.A. Sharp, *J. Electroanal. Chem.* **43** (1973) 9.
- T.J. Stone, W.A. Waters, *J. Chem. Soc.* (1964) 213.