Reduction of Dissolved Oxygen in Boiler Water Using New Redox Polymers

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ABSTRACT: New polymers were used as catalysts for the removal of dissolved oxygen in boiler water. These polymers, based upon hydroquinone-quinone redox system, were prepared by polymerization of methyl 4-(2,5-dimethoxybenzyl)cinnamate and copolymerization of this monomer with 4-(4′-vinylphenethyl)-1,10-phenanthroline. The resulting product was used to synthesize polymers containing transition metal ions. Nuclear magnetic resonance, infrared spectroscopy, and elemental analysis were achieved to characterize monomers and/or electron-transfer polymers. These polymers were used for the removal of oxygen from water. It was shown that the oxygen content was reduced to less than 0.1 mg L^{-1} in $\sim$ 70 s. Based on the obtained results, the redox capacity of two polymers were determined. It was established that the poly-4-(2,5-dihydroxybenzyl)cinnamic acid reached a redox capacity of 69.7 mg of O_2 per gram of polymer. © 2010 Wiley Periodicals, Inc. J Appl Polym Sci 118: 7–16, 2010

Key words: electron-transfer polymers; dissolved oxygen; hydroquinone; phenantroline

INTRODUCTION

Insoluble polymers are an important class of reagents developed for the halogenation,[1,2] oxidation,[3,4] hydrogenation,[5] reduction[6–8] of organic compounds or for the removal of oxygen from solutions.[9] Their usefulness arises from the ability to recycle the spent polymer[5] and from an easy reaction workup,[3,4,10,11] as the products of reaction can be isolated by filtration of the resin. These polymeric reagents always require the preparation of macromolecular backbone[12–21] or tedious modification of a commercial one.[1,2,10,11,22–24]

One of our research project concerns the syntheses of polymers based upon hydroquinone-quinone redox system to reduce dissolved oxygen in boiler water. In many studies, Electron-Transfer Polymers (ETP) are obtained by addition of redox functionalities to a preformed chloromethylated resin[25,26] or prepared by Friedel–Crafts alkylation of this system to styrene divinylbenzene copolymers.[27] Starting from the polymer backbone, four steps are necessary to synthesize the ETP but with only 60 to 80% of grafted redox functions.[25–27] Therefore, there is a need for new methods giving maximal density of redox functionalities. In this way, new polymerization methods have been applied for the preparation of controlled molecular weight polymers.[28–34] In the same context, we have recently described others strategies based upon alkylation and lithiation reactions and we have shown that it was possible to produce ETP with a high percentage of grafted redox functions (from 96 to 98 %) and polymers with one hydroquinone group per monomeric unit.[35] This point is very important because the corrosive effect of dissolved oxygen in boiler water requires the removal of oxygen to near-zero levels.

In our previous work, we have demonstrated that the redox properties of ETP were linked to the number of redox functions on the polymer matrix and we have shown that it was possible to reduce oxygen content of water to less than 0.5 ppm in $\sim$ 2.5 min using polyvinylbenzylhydroquinone.[35]

The aim of this work was to produce monomers described as being redox polymer precursors. After a detailed characterization of these monomers, ETP were obtained by polymerization or copolymerization. In this article, we wish to report results on the oxygen removal from water using the ETP. For an industrial application, redox capacities of the best ETP were determined and the turn over of one of them was studied.

EXPERIMENTAL

Materials

The synthesis of 4-methyl-1,10-phenanthroline was carried out by using 8-aminolepidine, glycerol, and
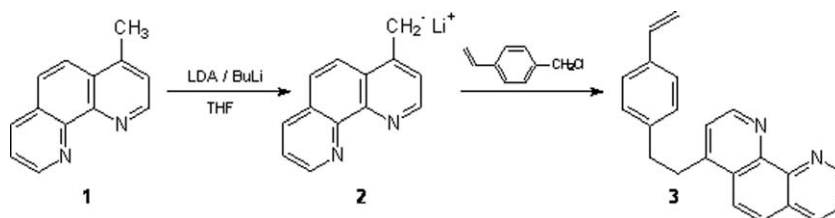
Scheme 1 Formation of 4-(4′-vinylphenethyl)-1,10-phenanthroline **3**.

sulphuric acid from Acros according to the protocol described by Lutun et al.[36] Sodium iodide, lithium isopropyl-amidure, palladium chloride, palladium diacetate, cobalt diacetate, and p-chloromethylstyrene came from Aldrich. 2,5-Dimethoxy-1-(4′-iodobenzyl)benzene was synthesized according to the protocol described in the literature.[37] Montmorillonite K_{10}, from Aldrich, was used without further purification before the preparation of catalyst according the preparation described by Ramchandani et al.[38] and Waterlot et al.[39]

Synthesis of monomers

Preparation of 4-(4′-vinylphenethyl)-1,10-phenanthroline

To a stirred solution of diisopropylamine (2.33 g, 23 mmol) in tetrahydrofurane (20 mL), butyllithium 2M (8.91 g, 23 mmol) was added (3 in Scheme 1). The mixture was cooled down to 0°C and stirred for 15 min. A solution of 4-methyl-1,10-phenanthroline (4 g, 22 mmol) in tetrahydrofurane (100 mL) was added dropwise. After 2 h at 0°C, the mixture was cooled to −15°C and a solution of 4-chloromethyl-styrene (3.36 g, 22 mmol) was slowly added. Then, stirring was continued for 24 h at room temperature. The crude product was quenched with water (60 mL) and organic layer was extracted with dichloromethane (3 × 150 mL), dried over Na_2SO_4 and concentrated under vacuum. The crude product was precipitated in dichloromethane (10 mL) and ethyl acetate (80 mL) mixture. Yield = 69%, m/z = 312.
 ^{1}H-NMR (CDCl$_3$): 2.96 (t, J = 7.6 Hz, 2H), 3.29 (t, J = 7.6 Hz, 2H), 5.14 (d, J = 10.9 Hz, 1H), 5.64 (d, J = 17.6 Hz, 1H), 6.61 (dd, J = 17.6 Hz, J = 10.9 Hz,

1H), 7.03 (d, J = 7.3 Hz, 2H), 7.25 (d, J = 6.5 Hz, 3H), 7.50 (dd, J = 7.9 Hz, J = 4.2 Hz, 1H), 7.66 (d, J = 9.1 Hz, 1H), 7.90 (d, J = 9.1 Hz, 1H), 8.10 (d, J = 7.9 Hz, 1H), 8.96 (d, J = 3.8 Hz, 1H), 9.11 (d, J = 4.2 Hz, 1H); ^{13}C-NMR (CDCl$_3$): 34.3, 36.1, 113.4, 122.0, 123.0, 123.2, 126.2, 126.4, 127.8, 128.1, 128.6, 135.8, 136.5, 140.3, 146.5, 147.0, 147.3, 149.9, 150.3; Elemental analysis of $C_{22}H_{18}N_2$, Calcd: C, 85.13 %; H, 5.85 %; O, 9.02%. Found: C, 85.12 %; H, 5.80 %; O, 9.08 %.
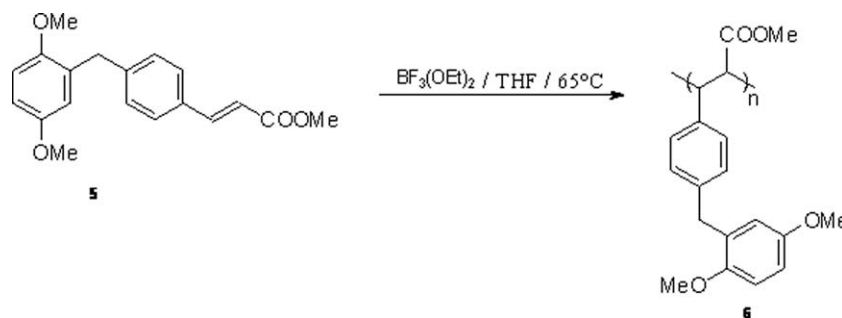
Preparation of methyl 4-(2,5-dimethoxybenzyl)cinnamate

A mixture of 2,5-dimethoxy-1-(4′-iodobenzyl)benzene **4** (15 g, 42.4 mmol), methyl acrylate (7.3 g, 84.8 mmol), carbonate de potassium (15.8 g, 114.3 mmol), catalyst K_{10}-Pd-Cu[39] (1.5 g), and 100 mL of dimethylformamide was refluxed for 2 h (5 in Scheme 2). The catalyst was collected and the cooled reaction mixture was stirred with 100 mL of water. The organic layer was extracted with dichloromethane (50 mL) and dried over $CaCl_2$. The organic solvents were removed and the product was purified in heptane to give the monomer **5**. Yield = 93%, white powder, m.p. = 83°C, m/z = 312.
   ^{1}H-NMR (CDCl$_3$): 3.72 (s, 3H), 3.76 (s, 3H), 3.79 (s, 3H), 3.95 (s, 2H), 6.38 (d, J = 16.1 Hz, 1H), 6.66 (d, J = 3.0 Hz, 1H), 6.72 (dd, J = 8.8 Hz, J = 3.0 Hz, 1H), 6.79 (d, J = 8.8 Hz, 1H), 7.22 (d, J = 8.1 Hz, 2H), 7.42 (d, J = 8.1 Hz, 2H), 7.66 (d, J = 16.1 Hz, 1H); ^{13}C-NMR (CDCl$_3$): 36.1, 51.7, 55.7, 56.0, 111.5, 116.9, 128.2, 128.4, 130.2, 132.1, 143.7, 144.9, 151.7, 153.6, 167.7; IR (KBr pellets): 2994, 2947, 2835, 1710, 1630, 1500, 1429, 1321, 1228, 1168, 1020; Elemental analysis of $C_{19}H_{20}O_4$, Calcd: C, 73.06 %; H, 6.45%. Found: C, 72.92 %; H, 6.29 %.
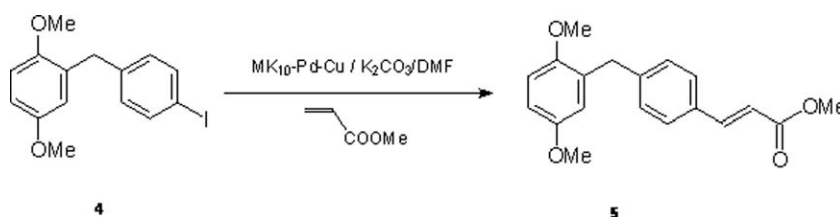
Scheme 2 Synthesis 4-(2,5-dimethoxybenzyl)cinnamate **5** from 2,5-dimethoxy-1-(4′-iodo-benzyl)benzene **4**.

Scheme 3 Formation of Poly-methyl-4-(2,5-diméthoxybenzyl)cinnamate 6.

Synthesis of electron-transfer polymers

Preparation of Poly-methyl-4-(2,5-dimethoxybenzyl)cinnamate

A solution of $BF_3(OEt)_2$ (14.6 g, 103 mmol) was added to a solution of methyl-4-(2,5-dimethoxybenzyl)cinnamate (8 g, 25.6 mmol) in tetrahydrofurane (50 mL) at room temperature (6 in Scheme 3). The mixture was stirred at 65°C for 48 h and was concentrated under vacuum. After washing the residue with a solution of $1M$ Na_2CO_3, the organic layer was extracted with dichloromethane (50 mL), dried over $CaCl_2$ and concentrated under vacuum to give 6 (6.5 g, 80%) as a brown solid.

Removal of blocking groups in polymer 6

Preparation of Poly-methyl-4-(2,5-dihydroxybenzyl)cinnamate. To a stirred solution of poly-methyl-4-(2,5-dimethoxybenzyl)cinnamate 6 (6.6 g, 2.11 mmol) was added a solution of 47% hydriodic acid (7 in Scheme 4). The mixture was stirred and heated at reflux temperature, 110°C for 16 h. The organic layer was washed with deionized water until the washing was neutral to pH paper, and then dried to constant weight. Polymer 7 was obtained as a brown powder. Yield = 73%.

Preparation of Poly-4-(2,5-dihydroxybenzyl)cinnamic acid. To a stirred solution of poly-methyl-4-(2,5-dimethoxy-benzyl)cinnamate 6 (6.6 g, 2.11 mmol) in dichloromethane (10 mL), a molar solution of boron tribromine (8.5 mL, 8.5 mmol) was added dropwise at room temperature and the mixture was heated to 40°C for 24 h (8 in Scheme 4). The mixture was poured into a hydrochloric acid solution $1M$ (50 mL) and the organic layer was extracted with dichloromethane (50 mL). The mixture was concentrated under vacuum and chloroform (25 mL) was added to the residue. Rapid crystallization of polymer occurred. After filtration, the polymer 8 was isolated. Yield = 75%.

Synthesis of copolymer 9

A solution of $BF_3(OEt)_2$ (2.13 g, 15 mmol) was added to a solution of methyl 4-(2,5-dimethoxybenzyl)cinnamate (2 g, 6.4 mmol) and 4-(4'-vinylphenethyl)-1,10-phenanthroline (2 g, 6.5 mmol) in tetrahydrofurane (25 mL) at room temperature. The mixture was stirred at 85°C for 12 h and was concentrated under
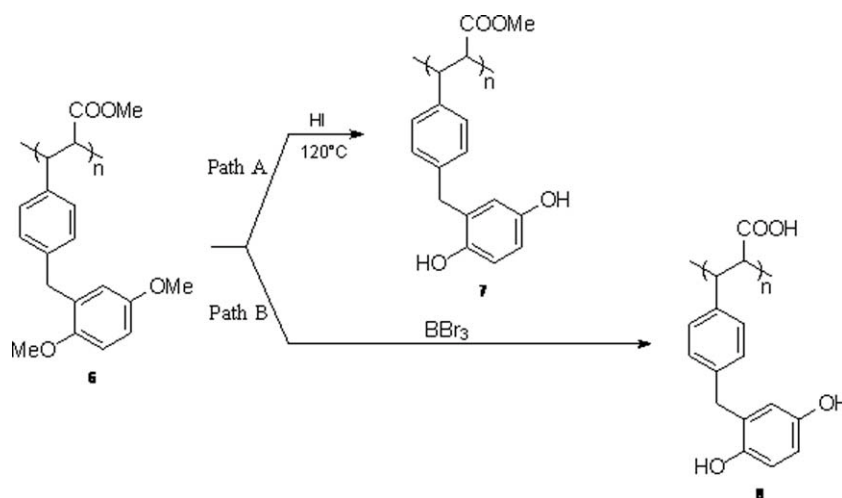
Scheme 4 Formation of Poly-methyl-4-(2,5-dihydroxybenzyl)cinnamate 7 and Poly-4-(2,5-dihydroxybenzyl)cinnamic acid 8.
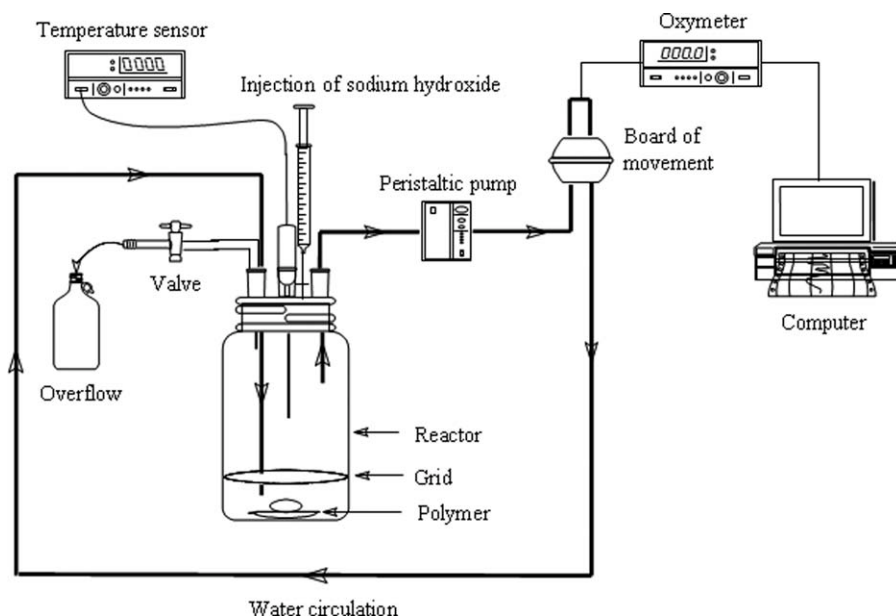
Figure 1 Shematic representation of the assembly for the reduction of dissolved oxygen in water.

vacuum. After adding a solution of BBr$_3$ (25 mL, 25 mmol) in dichloromethane to the residue, the mixture was stirred at 40°C for 12 h. The organic layer was washed with a solution of 1M HCl and was extracted with dichloromethane (50 mL), dried over CaCl$_2$ and concentrated under vacuum to give a brown oil. The copolymer **9** was obtained as a brown solid by addition of diethyl ether (100 mL) and filtration of the precipitate. Yield = 75%.

Preparation of copolymer 10 and 11

To a stirred solution of copolymer **9** (1 g, 1.8 mmol) in tetrahydrofurane (30 mL), Pd(OAc)$_2$ (0.56 g, 2.5 mmol) or Co(OAc)$_2$, 4H$_2$O (0.62 g, 2.5 mmol) was added, respectively. The mixture was stirred at room temperature for 12 h. After collecting, the precipitate was washed with tetrahydrofurane (20 mL) and water (2 × 20 mL). Copolymers **10** and **11** were obtained with good yields (90%).

Measurements

^{1}H-NMR 300 MHz spectra were run on a Bruker AC300 spectrometer with TMS as an internal reference. The products were dissolved in the mentioned solvent. Data are given in the following order: chemical shift in ppm, multiplicity (s, singlet; d, doublet; dd, double-doublet), coupling constant in Hertz, assignment. ^{13}C-NMR spectra were determined at 75 MHz with a Bruker AC300 spectrometer with TMS as an internal reference. The solvent used is indicated below. IR absorption spectra were recorded as solids in KBr pellets on a Bruker IFS48 Fourier transform spectrophotometer. The mentioned IR absorp-

tions were observed as strong bands in cm^{-1}. Elemental analyses were performed by "Service Central de Microanalyses" of CNRS, in Vernaison, France. These results, associated to the ^{1}H-NMR data, allowed us to determine the values for « p » and « q » for the reaction product. Melting points were determined with a Metler FP1 and are uncorrected. Mass spectra were obtained using fast atom bombardment on a Nermag R-10–10H spectrometer. Data are reported in the form m/z (intensity relative to base = 100).

The preparation of the tests was an important milestone for the accuracy and the reproducibility of measurements. Thus, deoxygenating tests conducted with hydroquinone, polymers and copolymers required a thorough cleaning of the materials (Fig. 1). Several steps were necessary before beginning the test:

1. Put the polymer in the bottom of the reactor and add a grid to retain the polymer in this reactor part during the agitation
2. Fill the reactor and the circuit with high-purity water, produced starting from distilled water using a Milli-QTM deionizing system (Millipore, Belford, MA). 334 mL of water were necessary for this operation
3. Chose a concentration of dissolved oxygen by bubbling air through the solution in the reactor. In this study, the concentration of dissolved oxygen was set at 8.4 mg L^{-1}
4. Add, with a syringe, a solution of sodium hydroxide (2.5M) after stabilization of the system (temperature and oxygen concentration) to adjust the pH of the solution (pH = 9).

Polymer	Melting point (°C)	Infrared band (cm^{-1}) KBr pellets	Elemental analysis (%)
6	79–80	2994, 2948, 2831, 1736, 1634, 1606, 1504, 1463, 1434, 1400, 1214, 1168, 1043	nd
7	nd	3224 (O—H), 2981, 2941, 1735, 1633, 1605, 1505, 1210	Calcd: C, 71.33%; H, 6.29%; O, 22,38% Found: C, 71.34%; H, 6.18%; O, 22,48%
8	nd	3482, 3224, 2891, 2941, 2600, 1716, 1633, 1605, 1505, 1210.	Calcd: C, 70.59%; H, 5.88%; O, 23.53% Found: C, 70.65%; H, 5.87%; O, 23.48%

nd: not determined.

RESULTS AND DISCUSSION

Synthesis of monomers

The key starting material for these syntheses was the 4-methyl-1,10-phenanthroline **1**,[40] obtained by the reaction between 8-aminolepidine and glycerol with sodium iodide and sulfuric acid.[36] Reaction of **1** with lithium isopropyl-amidure and p-chloromethyl-styrene led to the 4-(4′-vinylphenethyl)-1,10-phenanthroline **3** in a 69% yield after purification (Scheme 1).

The next step of the work was the synthesis of acrylate **5** by using a Heck reaction (Scheme 2). Starting from the 2,5-dimethoxy-1-(4′-iodobenzy)benzene,[37] the methyl 4-(2,5-dimethoxybenzyl)cinnamate **5** was obtained in a very good yield (93%) using the modified montmorillonite K$_{10}$ as catalyst. This one is a palladium and copper exchanged montmorillonite K$_{10}$ clay (K$_{10}$-Pd-Cu).[38,39]

Synthesis and characterization of polymers

The polymer **6** was synthesized by polymerization of specific monomer **5** (Scheme 3) and was obtained in a satisfactory yield (80%). No hydroxy group and carboxy function was identified by analysis of this polymer by FTIR [Table I and Fig. 2(b)]. Moreover, the IR studies have been carried out by focusing on three principal regions, viz., $>$C=O stretching (1750–1700 cm^{-1}), —C=C— stretching (1630 cm^{-1}) and the bending of ethylenic C—H (992 cm^{-1}). Before polymerization, the conjugated carbonyl and ethylenic functions were characterized by a band at 1710, 1630, and 992 cm^{-1}, respectively (Fig. 2). The final product show the total disappearance of —C=C— and ethylenic C—H bands and at the same time the intensity of the $>$C—O band at 1736 cm^{-1} appeared [compare Fig. 2(a,b)] indicating the success of the polymerization of monomer **5** to give polymer **6** in which the carbonyl function is not conjugated with a π ethylenic system.

The methoxy groups of polymer **6** were removed by addition of 47% hydriodic acid[41,42] to give the polymer **7** with a maximal density of hydroquinone on the polystyrene matrix (Scheme 4, path A). A second method was performed to cleave the methoxy groups of the polymer **6**. The cleavage reaction was achieved by addition of boron tribomine and the polymer **8** was isolated (Scheme 4, path B). The ETP **7** and **8** were obtained with 73 and 75% yields, respectively. The polymer structures were confirmed by FTIR and elemental analyses (Table I). The IR studies have been carried out by focusing on four principal regions, viz., —OH stretching of carboxylic function (3600–3400 cm^{-1}), —OH stretching of phenolic function (3400–3200 cm^{-1}), —C—H stretching of methoxy group (2820–2840 cm^{-1}), and —C—O— stretching of ester function (1160–1180 cm^{-1}) as changes occur only to these bands during the cleavage of methoxy groups. The comparison of FTIR spectra of the polymers **6** and **7** shows the appearance of —OH band at 3224 cm^{-1} and a diminution of bands characterizing methoxy groups. In the polymer **8**, the disappearance of these bands and the appearance of two bands at 3482 cm^{-1} and 2600 cm^{-1} show the formation of carboxylic function.

By using boron trifluoride etherate as reactant, we attempted to produce a copolymer using a mixture of 4-(4′-vinylphenethyl)-1,10-phenanthroline (**3**) and methyl 4-(2,5-dimethoxy-benzyl)cinnamate (**5**). A solution of boron trimomide was added after having concentrated the residue to cleave the methoxy groups. ETP **9** was isolated with 90% yield. The p and q values of this copolymer, $p = 4$ and $q = 1$ (Scheme 5, Table II), respectively, were determined by elemental and ^{1}H-NMR analyses. The spectra of this copolymer clearly showed a singlet at 3.51 ppm, assigned to the methylene protons. The triplets at 3.48 ppm (t, 2H, $J = 7.65$ Hz) and 3.06 ppm (t, 2H, $J = 7.54$ Hz) were respectively assigned to the aliphatic protons of the first and the second —CH$_2$— near the phenantroline group (Scheme 5).

During recent decades, palladium-quinone-catalyzed have been used in organic synthesis.[43–45] Lutun et al. described a copolymer of styrene and divinylbenzene containing substituted 1,10-phenanthroline
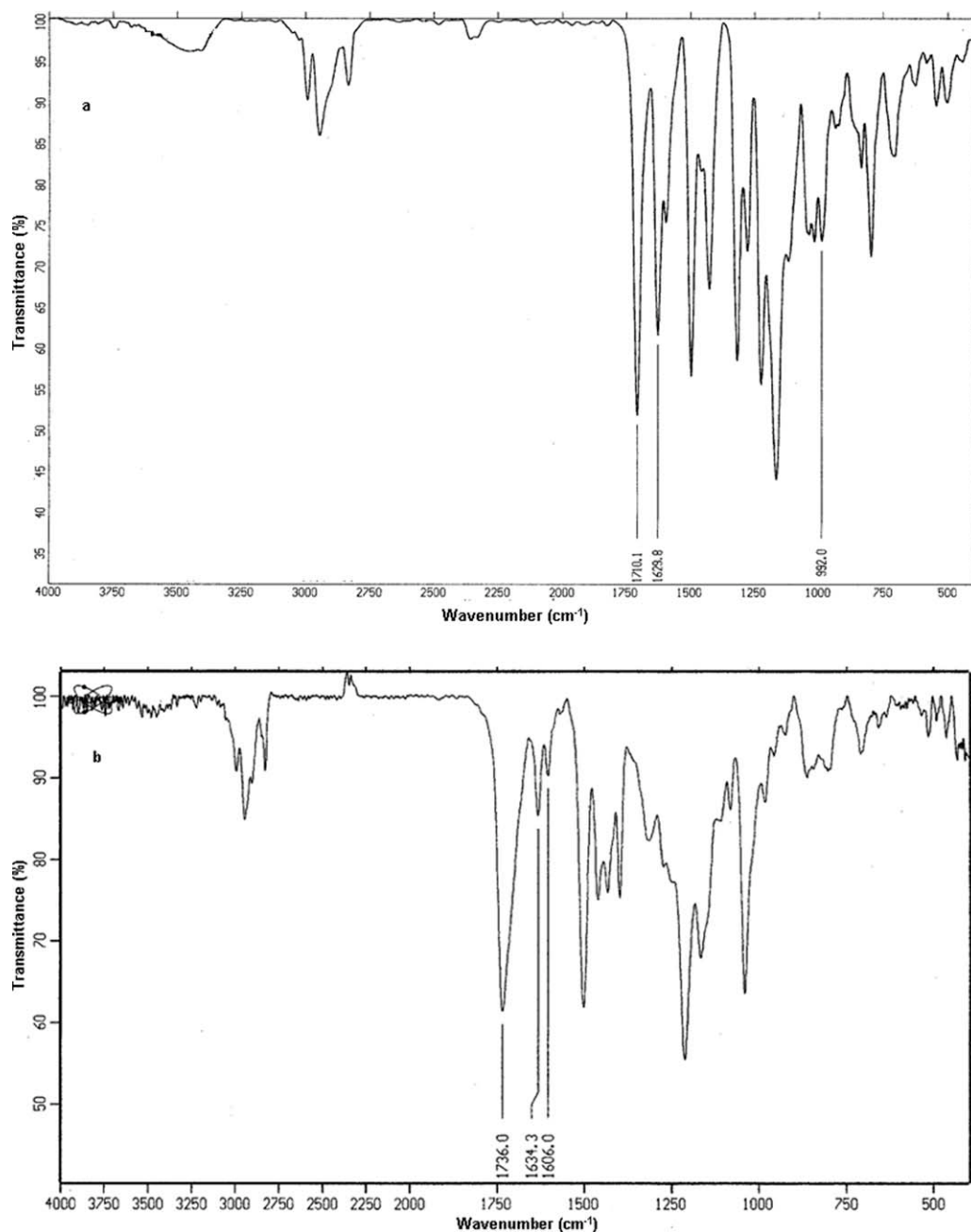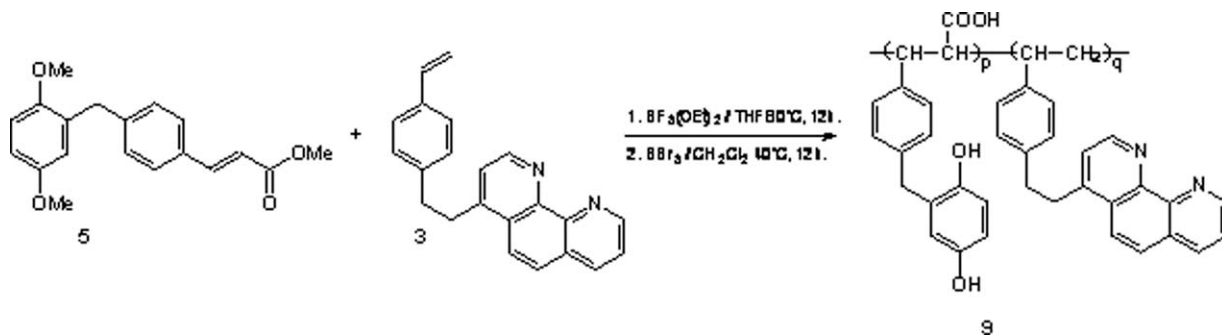
Figure 2 FTIR spectrum: (a) methyl 4-(2,5-dimethoxybenzyl)cinnamate **5**, (b) Poly-methyl-(2,5-dimethoxybenzyl)cinnamate **6**.

Scheme 5 Formation of copolymer **9** from 4-(2,5-dimethoxybenzyl)cinnamate **5** and 4-(4′-vinylphenethyl)-1,10-phenanthroline **3**.

TABLE II
Characteristics of Copolymers

| Polymer	Infrared band (cm^{-1}) KBr pellets	Elemental analysis (%)	indices value	Formula and average mass (g mol^{-1})
9	3424, 3245, 3016, 2917, 1652, 1561, 1522, 1414	Calcd: C, 74.12%; H, 5.50%; N, 2.01%; O, 18.37% Found: C, 74.19%; H, 5.78%; N, 1.97; O, 18.06%	$p = 4$ $q = 1$	C$_{86}$H$_{76}$N$_2$O$_{16}$ 1392
10	nd	Calcd: N, 1.76; Pd, 6.69% Found: N, 1.88%; Pd, 6.44%	$p = 4$ $q = 1$	C$_{90}$H$_{86}$N$_2$O$_{18}$Pd 1588
11	nd	Calcd: N, 1.82; Co, 3.82% Found: N, 1.82%; Co, 3.91%	$p = 4$ $q = 1$	C$_{90}$H$_{86}$N$_2$O$_{18}$Co 1541

nd: not determined.

10 years ago.[46] After a reaction with palladium diacetate, the authors have shown the stability of the copolymer to produce oxadiazoles. Moreover, using cobalt diacetate as complexant, reduction of dissolved oxygen in water was possible.[47] The authors explained their results by the good reactivity of cobalt-complex with oxygen.[48,49] Thus, copolymer **9** was complexed with palladium diacetate and cobalt diacetate tetrahydrate, according to the procedure described by Zhuangyu et al.,[50] to give copolymers **10** and **11** in satisfactory yields 90%, respectively (Scheme 6). Elemental analyses were performed to determine the formula of each of these polymers (Table II).

## Redox properties of the resins

Four different chemical structures of ETP were used to reduce dissolved oxygen in water. For this, air was first of all bubbled through a NaOH solution (pH = 9) to give [O$_2$] = 8.4 ppm (mg L^{-1}) and a hydroquinone to oxygen molar ratio (r) 2.5:1 was used. The mass of polymers **7**, **8**, **10**, and **11** added into the glass reactor (Fig. 1) were, respectively, 0.125, 0.119, 0.174, and 0.169 g. These mass were provided by the following equation:

$$m = \frac{[O_2]}{M_{O_2}} . V . r . \frac{M_{rd}}{n_{HQ}} \times 2,$$
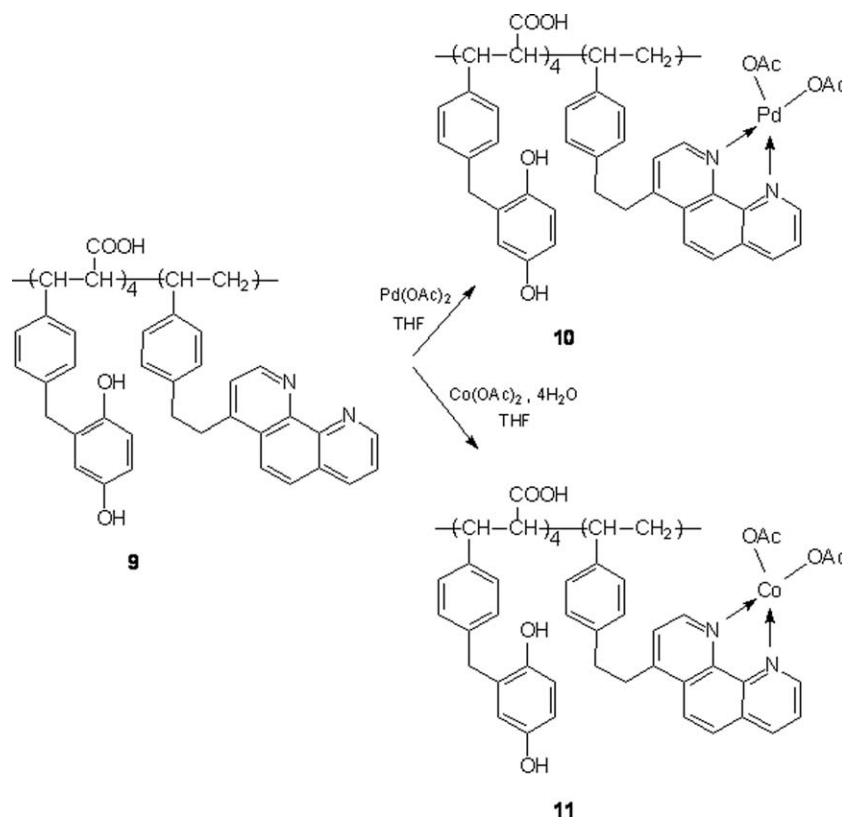
Scheme 6 Complexation of copolymer **9** by plomb diacetate and cobalt diacetate.

where $[O_2]$ is the desired value of the concentration of oxygen at the beginning of the test (see above), M_{O_2} is the molar mass of oxygen ($M_{O_2} = 32$ g mol^{-1}), V is the volume of high-purity water to fill the reactor and the circuit ($V = 334$ mL), r is the ratio described above, M_{rd} is the molar mass of macromolecules and n_{HQ} is the number of hydroquinone in the redox system. The factor 2 in the relation was explained by the properties of hydroquinone-quinone redox system to undergo electron transfer reactions according a bielectronic mechanism as illustrated in chemical reaction (1).

$$\tag{1}$$
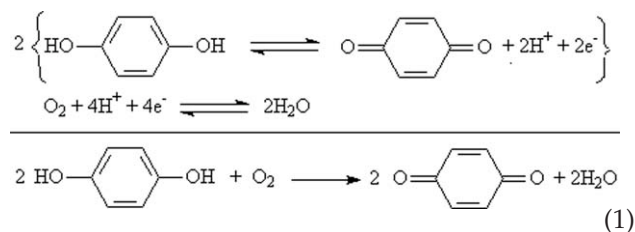
Many studies on the redox polymers containing hydroquinone units in the polymer chains have been published. The redox ability of ETP can be estimated by cyclic voltammetry,[30,51,52] but in most of studies electrochemical behavior was conducted via the determination of the redox potential by the Nernst equation with two considerations: the reversibility of the redox reactions at the electrode and the free from adsorption.[48] That is why oxidation of polymers often used by the authors are based on potentiometric titration method, using as an example the polymer in 90% aqueous acetic acid with bromine in 90% aqueous acetic acid.[53–56] The redox potential of specific redox polymers may be determined using others conditions, such as acetic acid with bromine and albumin in the same solvent[53,54] or acetic acid mixed with or without sulfuric acid-potassium sulfate buffer and titrated with ceric ammonium acetate in 90% of acetic acid.[18–20,57]

The redox properties of ETP can be studied through the determination of their redox capacity too. This notion defines the oxidation and reduction power of an ETP measured in milliequivalents (meq) and is referred to a mass (grams of dry product) or a volume (milliliters of swollen resin of defined grain size). It is in this context that the redox properties of specific polymers have been evaluated by Kun et al. using iodine, iron, cerium.[25–27] According to the redox capacity of their materials, the authors concluded that one area of interest of their polymers was the removal of oxygen from water and organic solvents.[25,26] Thus, for our purpose, the redox capacity of the ETP may be defined as the oxygen content reduced per gram of dry material after stabilization.

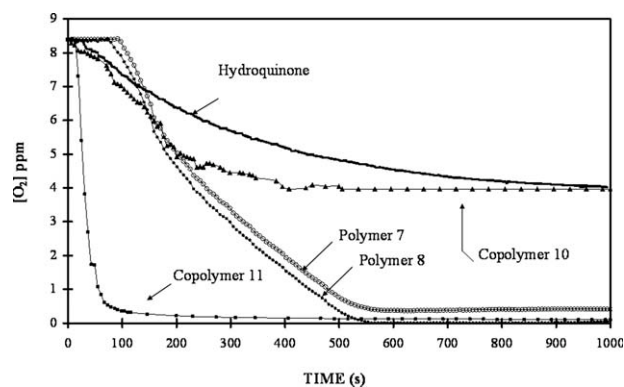Because the corrosive effect of dissolved oxygen in boiler water requires the removal of oxygen to near-

Figure 3 Oxygen removal from water by using Electron-Transfer Polymers.

zero levels, one area of our interest is the reduction of oxygen in water by the ETP. For our application, we report first of all the results obtained with our ETP and in a second time, the redox capacity of the tested materials. Figure 3 shows the rate of oxygen removal from water under basic condition for the four synthesized polymers in comparison with hydroquinone. The performances of the ETP were compared in term of equilibrium state. The results showed that more time was necessary for the polymers **7** and **8** to reduce oxygen at the beginning of the test in comparison with hydroquinone. These results can be explained, on one hand by the lower solubility of the macromolecules and we presume on the other hand that oxygen-removal functions of these polymers present a less accessibility than hydroquinone. However, the rate of oxygen consumption increased using the polymers **7** and **8** in comparison with hydroquinone. The brown color of the basic solution observed in the last case seems to lie in semiquinone and quinone formations. Therefore, the low concentration of reduced oxygen can be explained by a dimerization reaction. According to the literature,[58] an increase in quinone stability is reflected by an increase in the reactivity of the corresponding hydroquinone with quinone.

As shown in Figure 3, it appeared that the oxygen content was lower than 0.1 ppm at time of 550 s after the beginning of the reaction between oxygen and the polymer **8**. As contrast, the copolymer **10** is not recommended for reducing dissolved oxygen in water with a good redox capacity. Indeed, even if the rate of oxygen consumption was better than hydroquinone, the capacity to reduce oxygen reached the same plateau as hydroquinone: 4 ppm in 1000 s. The difference between the capacities of the ETP **8** and **10** for the removal of oxygen from water is surprising with regard to their chemical structure. Indeed, copolymer **10** also contained poly-4-(2,5-dihydroxybenzyl)cinnamic acid moieties with a content of 80% ($p = 4$, $q = 1$). The low reaction rate
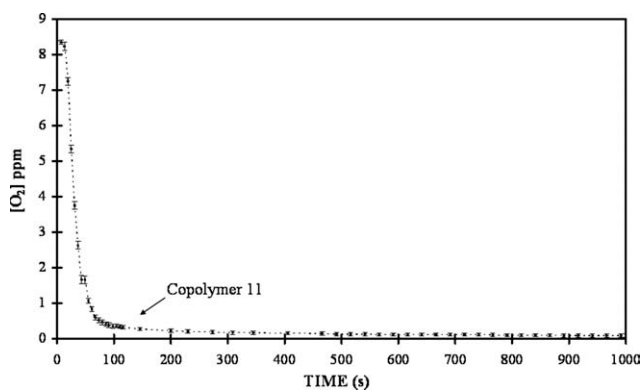
Figure 4 Mean (number of tests: $n = 4$) and standard deviation of oxygen removal from water by using copolymer **11**.

obtained with this copolymer can probably be explained by diffusional problems and/or lack of availability of redox sites in comparison with those in the polymer **8**. On the other hand, we can not exclude the possible reaction between palladium and hydroquinone[59] and as it was the case for the synthesis of oxadiazoles,[36] a decomposition of palladium occurred during the experiment inducing probably a decreasing of the reactivity of hydroquinone with dissolved oxygen.

The Figure 3 clearly shows that the polymer **8** and the copolymer **11** efficiencies were very similar (0.1 and 0.05 ppm, respectively). The capacity of copolymer **11** for the removal of dissolved oxygen became efficient more rapidly than that of the polymer **8**. For the first time, results seem to indicate that the oxygen content of water may be reduced to less than 0.5 ppm in $\sim$ 70 s. This result is in accordance with the previous work described in the literature[36,40] and confirms the reaction of cobalt-complex with dissolved oxygen in water. Moreover, for the deoxygenation experiment with copolymer **11**, turn over was studied after recycling according to the protocol described by Andries.[47] The results are gathered in
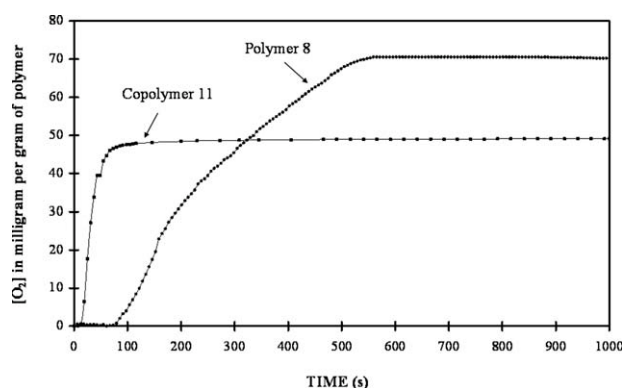

Figure 5 Redox capacity of the polymer **8** and the copolymer **11**.

Figure 4 and shows the reproducibility of the tests and the possibility for reusing the copolymer **11** after four regenerations. Finally, polymers **8** and copolymers **11** appeared to be the best polymers of those studied in our work. Their redox capacity was, respectively, evaluated as 69.7 and 49.4 mg of O_2 per gram of polymer (Fig. 5).

CONCLUSIONS

We investigated the synthesis of redox polymers and copolymers to reduce the dissolved oxygen in boiler water. For this purpose, it was established by using two of the four synthesized redox polymers that it was possible to remove dissolved oxygen from water to obtain very low concentration (<0.1 ppm). The first one was obtained by copolymerization of methyl 4-(2,5-dimethoxybenzyl)cinnamate with 4-(4′-vinylphenethyl)-1,10-phénanthroline and then complexed with cobalt ion after the removal of blocking group. This copolymer reached a redox capacity of 49.4 mg of O_2 per gram of polymer and showed a very high reproducibility for the removal of dissolved oxygen from water. The second one was the poly-4-(2,5-dihydroxybenzyl)cinnamic acid characterized by a high capacity to reduce dissolved oxygen in boiler water. Indeed, its redox capacity was evaluated as being 69.7 mg of O_2 per gram of polymer.

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