Synthesis, Characterization, and Electropolymerization of Mannich Bases: Influence of Substituents on Protective Ability of Organic Coatings

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ABSTRACT: Aminoalkyl phenol derivatives were prepared and tested for electrooxidation in alkaline hydroalcoholic electrolytes. We estimated the relative insulating character of thin (<0.3 μm) organic coatings on several metal electrodes (Fe, Cu, and Ni), through both voltammetric and potentiostatic runs. Unsaturated allyl and but-3-enyl groups confer the most effective passivation phenomenon, while N-methyl-substituted Mannich bases do not provide the good protective properties expected. This result was explained through the relative easiness of the nitrogen oxidation of these monomers, leading to parasite reactions (methoxylation of the growing polymer chains) and additional termination reactions, thereby limiting the molecular weight of the polymer. FTIRAS results showed that products of the anodic oxidative coupling process consist (especially for the nature of monomer) of a poly(oxy-1,4-phenylene)-type structure. Amino and unsaturated substituted groups remain unchanged during electropolymerization, making the resulting coatings attractive to use as reactive primer layers. The thickness of the coatings was found to reach 2–5 μm in free-water solutions. This behavior, particular to Mannich bases, was explained by the hydrophilic character of the growing polymer chains due to the presence of amino groups. © 2000 John Wiley & Sons, Inc. J Appl Polym Sci 75: 1054–1067, 2000

Key words: Mannich bases; polymer coatings; electropolymerization; corrosion; thin films

INTRODUCTION

The electropolymerization of phenols has been the focus of numerous studies during the last two decades. Applications using poly(phenylene oxide)-coated electrodes include the development of potentiometric sensors,[1] the insulation of submicron-sized carbon electrodes,[2] and corrosion protection for metals.[3] The intrinsic, nonconducting nature of such coatings was found to be a problem for the buildup of thick (several micrometers) polymeric films developed to compete with current electrophoretic paints. Nevertheless, Mengoli et al. were able to form films dozens of micrometers thick using either aliphatic amine (usually allylamine)[4] or ammonia[5] to give the phenol hydroalcoholic solution a pH near 10. The amine is considered to enter into competitive adsorption onto the metal surface[6] and to enhance the bulk conductivity of the growing polymer chain by increasing the hydrophile character of the chain.[5] The amine facilitates the passage of the electropolymerization current, producing thick organic coatings. Even though organic amines are, in part, directly bound to polyether chains,[7] some residual amine is trapped in the polymer network. Its dissolution, when rinsing the barely formed coating or its evaporation (during the usual thermal cure of the coating), can cause irreversible defects, creating conductive
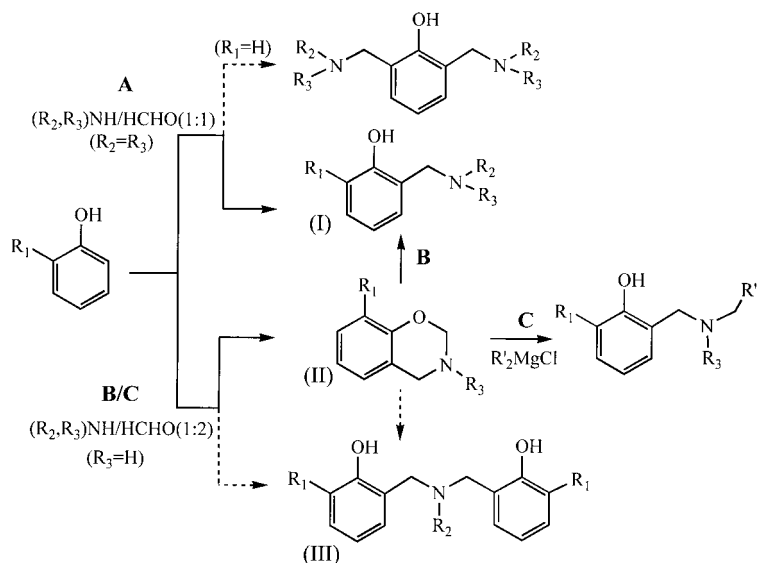
Scheme 1

paths and, hence, poorly protective features (considering that it is fairly thick). This major drawback can be overcome by covalently linking the hydrophilic amine function to the phenol monomer. Under these circumstances, Mannich bases are useful starting materials for electrosynthesizing poly(phenylene oxide) films. Furthermore, aminomethyl phenol derivatives efficiently inhibit steel corrosion in acid media[8] and are suitable as water-soluble polymers for cathodic electrodeposition.[9]

The protective ability of the electrochemically polymerized films can be controlled by a variety of parameters, including the nature of the solvent or electrolyte and the electrodeposition solution pH. Until now, the relationship between the structure of the phenol monomer and the corrosion resistance of the coated metals has been scarcely investigated, phenols being limited to common commercial compounds.[3,4]

In this article, the synthesis and characterization of a series of new Mannich bases is reported. The starting phenol is either unsubstituted or *ortho*-substituted, so as not to impede polymer-chain propagation through head-to-tail C—O coupling. Unsaturated substituents (allyl and but-3-enyl) are largely envisaged as they are easily heat-crosslinked.[10] N-Methyl-substituted monomers are also synthesized since the electron-donating methyl groups, by concentrating the unshared pair of the base on the nitrogen atom, are expected to favor Lewis acid–base interactions between the monomer and anode metal, thereby improving coating/metal adhesion.

We describe the formation of nonconductive polymer films on the electrochemical oxidation of such substituted Mannich bases. The relative insulating character of coated metal anodes were investigated using electrochemical measurements. Results about the monomer structure are discussed.

EXPERIMENTAL

Materials

Methanol (Carlo Erba) was freshly distilled; water was purified with a Millipore system. The other chemical reagents were purchased from Merck and Aldrich (Milwaukee, WI) (reagent grade) and used as supplied. The synthesized Mannich bases were stored at $0-4°C$ and used within 15 days of formation or purification.

Synthesis of Monomers (Scheme 1)

Path A: Condensation of a Phenol Derivative with Formaldehyde and a Secondary Amine[11,12]

The appropriate amine (0.60 mol) was added, by stirring drop by drop, to a solution of paraformaldehyde* (0.60 mol) and KOH (6 mmol) in 30 mL of methanol at a temperature below 25°C. Then, the phenol (0.62 mol) was added portionwise and the reaction mixture heated under reflux for 40 min. The cooled solution was treated with 15% HCl.

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* Paraformaldehyde that depolymerized in base was used as a source of formaldehyde.[11]

The residual starting phenol was then extracted with ether and the soluble hydrochloride solution neutralized with a saturated potassium carbonate solution. The free-base was extracted with ether and isolated in the usual way.[11] The yellow oil residue was found to give undesired by-products (additional small peaks in the ^{1}H-NMR spectrum). Vacuum distillation gave an almost colorless oil with satisfactory spectroscopic data.

Paths B and C: Synthesis of Benzoxazines

3,4-Dihydro-2H-1,3-benzoxazines were prepared from phenols, formaldehyde, and primary amines in a molar ratio of 1 : 2 : 1, respectively. The reaction was carried out as above (see path A). After adding the phenol, the reaction mixture was refluxed for 20 min. The resulting syrup dissolved in ether was treated with 5% aqueous KOH solution to remove unreacted phenol, amine, and formaldehyde. Benzoxazine was isolated as a lightly yellow-colored oil from the ether extract in the usual way.[12] Unlike other benzoxazines, 3,4-dihydro-3-allyl-2H-1,3-benzoxazine (contaminated by the bishydroxybenzylamine) was distilled under a vacuum prior to subsequent reactions.

Path B: Acidic Decomposition of Benzoxazines[12]

Mannich bases were prepared by liberating formaldehyde from a boiled acidic solution of benzoxazine in ethanol using the Burke[12] procedure. The crystallized hydrochloride was not isolated, thus impeding spectroscopic evidence of its structure.

Path C: Reaction of Organomagnesium Compounds with Benzoxazines[13]

A solution of benzoxazine (0.15 mol) in 50 mL of ether was added portionwise with cooling (below 5°C) to a solution of 3-propene magnesium chloride (0.35 mol) in 150 mL of ether (prepared by standard procedures). After all the benzoxazine was added, the solution was refluxed for 40 min. The cooled mixture was hydrolyzed with ammonium chloride and extracted twice with ether. The ethereal extract was dried over sodium sulfate. The removal of ether gave the Mannich base as an almost colorless oil having satisfactory spectroscopic data.

Spectral Data for Prepared Benzoxazines

^{1}H-NMR spectra were recorded in CDCl$_3$ containing tetramethylsilane as an internal standard on a Bruker 200 MHz NMR spectrometer. The sig-

nals are defined as s: singlet, d: doublet, dd: doubled doublet, t: triplet, q: quadruplet, and m: multiplet. The spin–spin coupling constants (in Hz) of the allylic system are described using the designations of the protons as indicated in the following formula: CH$_2$(a)=CH(b)—CH$_2$(c)—.

^{1}H-NMR data for **1**: δ 3.40(d, J$_{b-c}$ = 6.6, NCH$_2$CH, 2H), 3.98(s, NCH$_2$C, 2H), 4.88(s, OCH$_2$N, 2H), 5.21(dd, J$_{a-b\ cis}$ = 9.9, J$_{a-gem}$ = 1.5, CH$_2$CH, 1H), 5.25(dd, J$_{a-b\ trans}$ = 18.4, CH$_2$CH, 1H), 5.88(m, CH$_2$CHCH$_2$, 1H), 6.85–7.15(m, arom., 4H); **2**: δ 2.60(s, CH$_3$N, 3H), 3.97(s, NCH$_2$C, 2H), 4.90(s, OCH$_2$N, 2H), 6.80–7.20(m, arom., 3H); **3**: δ 3.38(d, J$_{b-c}$ = 7.5, NCH$_2$CH, 2H), 4.01(s, NCH$_2$C, 2H), 4.99(s, OCH$_2$N, 2H), 5.20(dd, J$_{a-b\ cis}$ = 10.0, J$_{a-gem}$ = 1.6, CH$_2$CH, 1H), 5.23(dd, J$_{a-b\ trans}$ = 16.8, CH$_2$CH, 1H), 5.90(m, CH$_2$CHCH$_2$, 1H), 6.80–7.20(m, arom., 3H); **4**: δ 2.21(s, CH$_3$C, 3H), 3.38(d, J$_{b-c}$ = 6.8, NCH$_2$CH, 2H), 3.95(s, NCH$_2$C, 2H), 4.90(s, OCH$_2$N, 2H), 5.18(dd, J$_{a-b\ cis}$ = 9.4, J$_{a-gem}$ = 1.5, CH$_2$CH, 1H), 5.22(dd, J$_{a-b\ trans}$ = 18.8, CH$_2$CH, 1H), 5.88(m, CH$_2$CHCH$_2$, 1H), 6.80–7.00(m, arom., 3H); **5**: δ 2.60(s, CH$_3$N, 3H), 3.36 (d, J$_{b-c}$ = 7.5, CCH$_2$CH, 2H), 3.98(s, NCH$_2$C, 2H), 4.82(s, OCH$_2$N, 2H), 5.03(dd, J$_{a-b\ cis}$ = 9.1, J$_{a-gem}$ = 1.7, CH$_2$CH, 1H), 5.06(dd,j J$_{a-b\ trans}$ = 16.1, CH$_2$CH, 1H), 6.08(m, CH$_2$CHCH$_2$, 1H), 6.80–7.00(m, arom., 3H); **6**: δ 3.32(d, J$_{b-c}$ = 7.2, NCH$_2$CH or CCH$_2$CH†, 2H), 3.34(d, J$_{b-c}$ = 7.0, NCH$_2$CH or CCH$_2$CH, 2H), 4.00(s, NCH$_2$C, 2H), 4.90(s, OCH$_2$N, 2H), 5.02[dd, J$_{a-b\ cis}$ = 11.5, J$_{a-gem}$ = 1.6, CH$_2$CH(CH$_2$C), 1H], 5.05[dd, J$_{a-b\ trans}$ = 17.2, CH$_2$CH(CH$_2$C), 1H], 5.20[dd, J$_{a-b\ cis}$ = 10.7, J$_{a-gem}$ = 1.5, CH$_2$CH(CH$_2$N), 1H], 5.23[dd, J$_{a-b\ trans}$ = 17.1, CH$_2$CH(CH$_2$N), 1H], 5.92(m, CH$_2$CHCH$_2$, 2H), 6.80–7.00(m, arom., 3H).

General features of IR spectra (thin films). No bands above 3200 cm^{-1}; ν‡(C—H)$_{allyl.}$ at 3075–3078 cm^{-1} (except **2**); ν(C—H)$_{CH2\ and\ CH3}$ at 2800–3000 cm^{-1}; skeletal ring breathing modes near 1600, 1580, and 1460–1490 cm^{-1}; ν(C—O)$_{Ar—O—CH2}$ at 1210–1230 and 1070–1080 cm^{-1}. The clearly separate band near 1580 cm^{-1} can be assigned as one of a degenerate pair and gives further evidence of the formation of the fused oxazine ring.[14]

Spectral Data for Prepared o-Aminomethyl Phenols

^{1}H-NMR data for **7**: δ 3.11(d, J$_{b-c}$ = 6.8, NCH$_2$CH, 4H), 3.70(s, NCH$_2$C, 2H), 5.13(dd, J$_{a-b\ trans}$ = 18.4, J$_{a-gem}$ = 1.7, CH$_2$CH, 1H), 5.18(dd, J$_{a-b\ cis}$ = 9.3, CH$_2$CH, 1H), 5.85(m, CH$_2$CHCH$_2$, 2H), 6.80–7.10(m, arom.,

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† The two doublets at 3.32 and 3.34 ppm appeared as a distorted triplet and could not be unequivocally assigned.
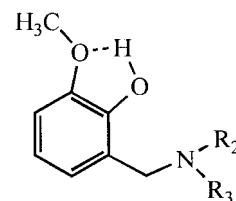‡ ν: stretching vibration.

4H); **8**: δ 2.34(s, CH$_3$N, 6H), 3.63(s, NCH$_2$C, 2H), 6.90–7.20(m, arom., 4H); **9**: δ 3.15(d, J$_{b-c}$ = 6.7, NCH$_2$CH, 4H), 3.75(s, NCH$_2$C, 2H), 3.85(s, CH$_3$O, 3H), 5.20(dd, J$_{a-b\,trans}$ = 17.1, J$_{a-gem}$ = 1.7, CH$_2$CH, 2H), 5.23(dd, J$_{a-b\,cis}$ = 10.3, CH$_2$CH, 2H), 5.88(m, CH$_2$CHCH$_2$, 2H), 6.60–6.75(m, arom., 3H); **10**: δ 2.32(s, NCH$_3$, 6H), 3.64(s, NCH$_2$C, 2H), 3.88(s, CH$_3$O, 3H), 6.60–6.75(m, arom., 3H); **11**: δ 3.11(d, J$_{b-c}$ = 6.7, NCH$_2$CH, 4H), 3.32(d, J$_{b-c}$ = 6.1, CHCH$_2$C, 2H), 3.70(s, NCH$_2$C, 2H), 4.98[dd, J$_{a-b\,cis}$ = 9.5, J$_{a-gem}$ = 1.6, CH$_2$CH(CH$_2$C), 1H], 5.01[dd, J$_{a-b\,trans}$ = 17.3, CH$_2$CH(CH$_2$C), 1H], 5.12[dd, J$_{a-b\,trans}$ = 18.2, J$_{a-gem}$ = 1.7, CH$_2$CH(CH$_2$N), 2H], 5.15[dd, J$_{a-b\,cis}$ = 9.7, CH$_2$CH(CH$_2$N), 2H], 5.85(m, CH$_2$CHCH$_2$, 3H), 6.70–6.95(m, arom., 3H); **12**: δ 2.27(s, CH$_3$N, 6H), 3.39(d, J$_{b-c}$ = 6.4, CHCH$_2$C, 2H), 3.60(s, NCH$_2$C, 2H), 5.06(dd, J$_{a-b\,cis}$ = 10.8, J$_{a-gem}$ = 1.9, CH$_2$CH, 1H), 5.09(dd, J$_{a-b\,trans}$ = 17.6, CH$_2$CH, 1H), 6.04(m, CH$_2$CHCH$_2$, 1H), 6.75–7.05(m, arom., 3H); **13**: δ 3.27(d, J$_{b-c}$ = 6.7, NHCH$_2$CH, 2H), 3.96(s, NHCH$_2$C, 2H), 5.18(dd, J$_{a-b\,cis}$ = 8.8, J$_{a-gem}$ = 1.7, CH$_2$CH, 1H), 5.21(dd, J$_{a-b\,trans}$ = 17.3, CH$_2$CH, 1H), 5.89(m, CH$_2$CHCH$_2$, 1H), 6.80–7.20(m, arom., 4H); **15**: δ 3.32(d, J$_{b-c}$ = 6.7, NHCH$_2$CH, 2H), 4.03(s, NHCH$_2$C, 2H), 5.18(dd, J$_{a-b\,cis}$ = 9.0, J$_{a-gem}$ = 1.7, CH$_2$CH, 1H), 5.21(dd, J$_{a-b\,trans}$ = 16.0, CH$_2$CH, 1H), 5.90(m, CH$_2$CHCH$_2$, 1H), 6.20–7.20(m, arom., 3H); **16**: δ 2.20(s, CH$_3$C, 3H), 3.20(d, J$_{b-c}$ = 6.6, NHCH$_2$CH, 2H), 3.89(s, NHCH$_2$C, 2H), 5.11(dd, J$_{a-b\,cis}$ = 10.0, J$_{a-gem}$ = 1.9, CH$_2$CH, 1H), 5.14(dd, J$_{a-b\,trans}$ = 16.7, CH$_2$CH, 1H), 6.70–7.00(m, arom., 3H); **17**: δ 2.42(s, CH$_3$NH, 3H), 3.37(d, J$_{b-c}$ = 6.2, NHCH$_2$CH, 2H), 3.68(s, NH, 1H), 3.88(s, NHCH$_2$C, 2H), 5.05(dd, J$_{a-b\,cis}$ = 9.5, J$_{a-gem}$ = 1.7, CH$_2$CH, 1H), 5.09(dd, J$_{a-b\,trans}$ = 17.5, CH$_2$CH, 1H), 6.04(m, CH$_2$CHCH$_2$, 1H), 6.75–7.00(m, arom., 3H); **18**: δ 2.32(q, CH$_2$CH$_2$CH, 2H), 2.65(t, NCH$_2$CH$_2$, 2H), 3.18(d, J$_{b-c}$ = 6.7, NCH$_2$CH, 2H), 3.78(s, NCH$_2$C, 2H), 5.06{dd, J$_{a-b\,cis}$ = 10.4, J$_{a-gem}$ = 1.8, CH$_2$CH[(CH$_2$)$_2$N], 1H}, 5.09{dd, J$_{a-b\,trans}$ = 18.4, CH$_2$CH[(CH$_2$)$_2$N], 1H}, 5.21[dd, J$_{a-b\,trans}$ = 15.7, J$_{a-gem}$ = 1.7, CH$_2$CH(CH$_2$N), 1H], 5.23[dd, J$_{a-b\,cis}$ = 8.3, CH$_2$CH(CH$_2$N), 1H], 5.85(m, CH$_2$CHCH$_2$, 2H), 6.80–7.15(m, arom., 4H); **19**: δ 2.25(s, CH$_3$C, 3H), 2.35(q, CH$_2$CH$_2$CH, 2H), 2.63(t, NCH$_2$CH$_2$, 2H), 3.15(d, J$_{b-c}$ = 6.8, NCH$_2$CH, 2H), 3.78(s, NCH$_2$C, 2H), 5.08{dd, J$_{a-b\,cis}$ = 9.8, J$_{a-gem}$ = 1.7, CH$_2$CH[(CH$_2$)$_2$N], 1H}, 5.10{dd, J$_{a-b\,trans}$ = 18.2, CH$_2$CH[(CH$_2$)$_2$N], 1H}, 5.22(dd, J$_{a-b\,trans}$ = 15.8, J$_{a-gem}$ = 1.7, CH$_2$CH(CH$_2$N), 1H], 5.25[dd, J$_{a-b\,cis}$ = 8.4, CH$_2$CH(CH$_2$N), 1H], 5.86(m, CH$_2$CHCH$_2$, 2H), 6.80–7.05(m, arom., 3H); **20**: δ 2.21(s, CH$_3$N, 3H), 2.25(q, CH$_2$CH$_2$CH, 2H), 2.51(t, NCH$_2$CH$_2$, 2H), 3.33(d, J$_{b-c}$ = 6.4, CCH$_2$CH, 2H), 3.65(s, NCH$_2$C, 2H), 5.03(dd, CH$_2$CH, 4H), 5.85(m, CH$_2$CHCH$_2$, 2H), 6.70–7.00(m, arom., 3H); **21**: δ 2.30(q, CH$_2$CH$_2$CH, 2H), 2.61(t, NCH$_2$CH$_2$, 2H), 3.12(d, J$_{b-c}$ = 6.7, NCH$_2$CH, 2H), 3.38(d, J$_{b-c}$ = 6.2, CCH$_2$CH, 2H), 3.78(s, NCH$_2$C, 2H), 5.03{dd, J$_{a-b\,cis}$ = 10.7, J$_{a-gem}$ = 1.8, CH$_2$CH(CH$_2$C) and CH$_2$CH[(CH$_2$)$_2$N], 2H}, 5.06{dd, J$_{a-b\,trans}$ = 18.6, CH$_2$CH(CH$_2$C) and CH$_2$CH[(CH$_2$)$_2$N], 2H}, 5.19[dd, J$_{a-b\,trans}$ = 16.2, J$_{a-gem}$ = 1.7, CH$_2$CH(CH$_2$N), 1H],

5.21[dd, J$_{a-b\,cis}$ = 8.7, CH$_2$CH(CH$_2$N), 1H], 5.88(m, CH$_2$CHCH$_2$, 3H), 6.70–7.00(m, arom., 3H).

General features of IR spectra (thin films). The synthesized Mannich bases exhibit a broad OH absorption band extending from 3300 to 2500 cm^{-1} and superimposed on the C—H stretching absorption. The absorption range of ν(O—H) confirms the formation of a chelate compound (**IV**) through an intramolecular H bond,[14] showing that aminomethylation occurred at the position *ortho* to the hydroxy group:

$$\tag{1}$$
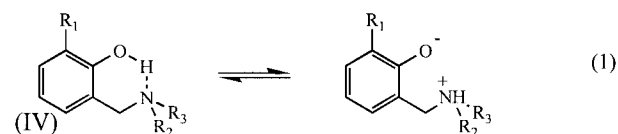
An additional and low intense ν(O—H) band near 3415 cm^{-1} for the methoxy-substituted Mannich bases **9** and **10** can be ascribed to the occurrence of a weaker OH $\cdots$ O intramolecular H bond[15] related to the following five-membered ring structure:

For the secondary amines **13–17**, the NH stretching vibration gives two bands in the narrow range 3300–3340 cm^{-1}, clearly suggesting the presence of the NH$_2^+$ group due to an equilibrium as in eq. (1).

Electrodes

For electrochemical runs, iron, copper, and nickel electrodes were embedded in a chemically inert epoxy resin (Serifix Struers) with 0.7, 0.5, and 1.1-cm^2 surface areas, respectively. Before each experiment, the electrode was mechanically polished from grade 400 to grade 1200, degreased by acetone (under ultrasonic agitation), and then air-dried. For FTIRRAS and thickness measurements, the working electrode was an optically polished rectangular sheet of brass (Masson & Cie, France) with an immersed area of 20 cm^2 and simply degreased in acetone.

Electrochemical Polymerization

The voltammetric and potentiostatic runs were performed at 25°C in a three-electrode cell; a sat-

urated calomel electrode (sce) was always used as the reference electrode. The apparatus and procedure were described in a previous article.[16] In this work, all potentials given are referenced to the sce.

The electrolysis solution was a water–methanol (20 : 80 v/v) solution containing $0.3M$ KOH and $0.1M$ Mannich base unless stated otherwise. These strongly alkaline and additive-free conditions were preferred to fairly alkaline ones (even though fairly alkaline conditions usually give thicker coatings[13]) and should facilitate the approach concerning the relationship between the monomer and the insulating character of the coatings. The high methanol content was fixed by the expected low solubility of Mannich bases in alkaline aqueous solutions.[17]

Figure 1 shows typical voltammograms recorded at low sweep rate (150 mV min^{-1}) and current decay curves. The nickel voltammogram obtained with **18** [Fig. 1(a)] consists of an initial oxidation reaction from the potential E_{ox} (described as in ref. 18 by the bottom of the oxidation wave) up to the peak potential E_p preceding a significant current flow suppression attributed to the buildup of a polymer layer. The residual current remains fairly constant over a potential range ΔE, beyond which a sharp increase in current was observed due to oxygen evolution and/or oxidation of the metal substrate.

The cyclic potential sweep was also performed in the no-breaking potential range of the coating [Fig. 1(b)]. The i_{p2}/i_{p1} ratio was measured, where i_{p1} and i_{p2} correspond to the value of the peak current during the first and second anodic sweeps, respectively.

Lastly, electropolymerizations were carried out under the constant potential E_p, giving the residual current i_{res} after 20 min of electrolysis [Fig. 1(c)]. A 200-mL solution was prepared for all the monomers and metal anodes investigated. Each electropolymerization experiment was repeated three times, giving differences between measured potentials (E_{ox} and E_p) less than 10 mV, while relative current differences for i_{res} were below 5%.

Characterization Techniques of Polymer Films

For this study, Fourier transform infrared reflection–absorption spectroscopy (FTIRAS) was especially suitable due to the low thickness of prepared polymer films (<300 nm).[19] Spectra were recorded on a Bruker IFS 66 spectrometer equipped with a triglycine sulfate detector and a
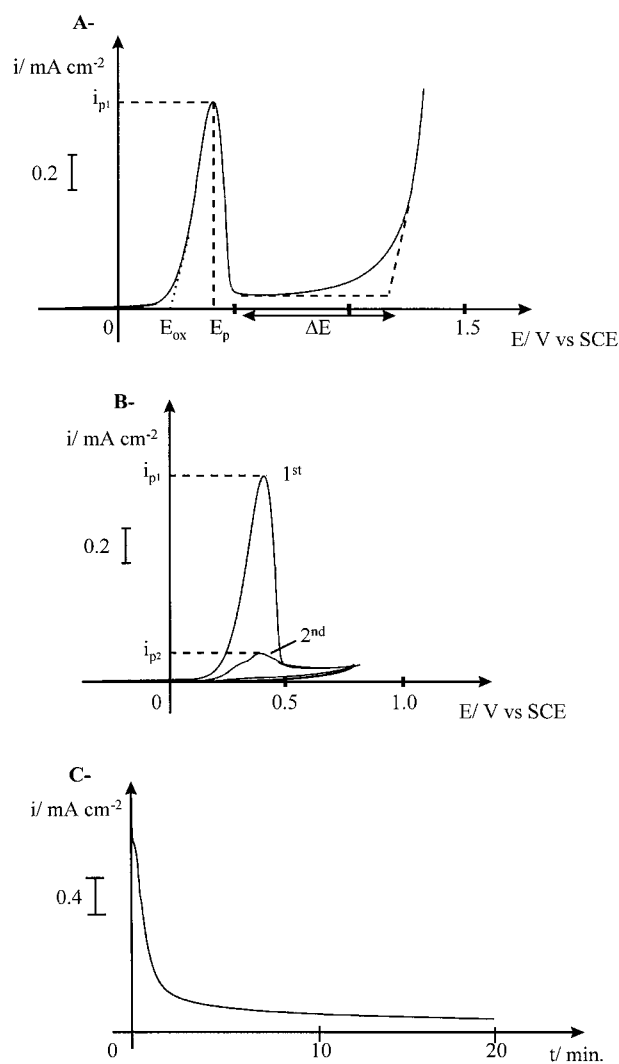
Figure 1 Typical electrochemical curves for Mannich bases (**18**) ($0.1M$) on nickel electrode in a $0.3M$ KOH water–methanol (20 : 80 v/v) solution. (A) Current-potential curve with an anodic limit beyond the breakdown potential of the film (scan rate: 150 mV min^{-1}). (B) Current-potential curves in the no-breaking potential range of the film; (1st) first sweep; (2nd) second sweep (scan rate: 150 mV min^{-1}). (C) Current decay curve (applied voltage: E_p).

reflection accessory, at a fixed angle of incidence of 80°. p-Polarized radiation was used to enhance the signal-to-noise ratio.[19] Each sample was purged with dry air for 20 min to minimize the absorption from water vapor and CO_2. Spectra were obtained from an average of 200 scans at a 4-cm^{-1} resolution. Before the coating process, the spectrum of the cleaned and uncoated electrode was recorded as a reference. Surface reflection spectra were obtained by digitally subtracting the spectrum of the clean brass plate from that with a

Table I   3,8-Disubstituted-3,4-dihydro-2H-1,3 Benzoxazines
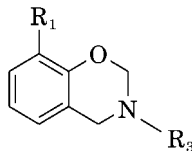
Compound No.	R_1	R_3	Yield[a] (%)	Boiling Point (°C/mmHg)
1	H	CH_2—CH=CH_2	60[b]	73/1
2	Cl	CH_3	9	99/4
3	Cl	CH_2—CH=CH_2	32	85/0.7
4	CH_3	CH_2—CH=CH_2	67	84/0.8
5	CH_2—CH=CH_2	CH_3	62	81/0.8
6	CH_2—CH=CH_2	CH_2—CH=CH_2	81	101/0.9

[a] Yields of isolated compounds with satisfactory spectroscopic data.
[b] *N,N*-Bis-(2-hydroxybenzyl)allylamine is also isolated in 20% yield.

polymer film on it. The thickness of the electrodeposited polymer films was estimated with a Talystep Taylor–Hobson apparatus through displacement of a sprung tungsten tip.

RESULTS AND DISCUSSION

Synthesis of Monomers

Except for **8**,[20] the synthesized benzoxazines and Mannich bases (Tables I and II) are not reported in the literature. Therefore, we confirmed their structure using ^{1}H-NMR and IR spectroscopy (see details in the Experimental section). Except for the condensation of phenol, formaldehyde, and dimethylamine, only the substituted 2-aminomethyl phenol (**I**) is isolated through path A (Scheme 1).

The reaction involving dihydrobenzoxazines (**II**) (paths B and C) is often preferred to the direct synthesis method (path A). If an *N*-methylol Mannich base is considered as an intermediate in the preparation of benzoxazine, a competitive reaction consists of the electrophilic attack on the *ortho* position of another molecule of the phenol to yield the bis(hydroxybenzyl)amine (**III**).[21] Thus, we replaced the 2-methoxy group in 2-methoxy phenol (path A) with chlorine, as the latter should be unfavorable to the latter side reaction by lowering the electron density at the free *ortho* position of the phenol. Except for the condensation of phenol with formaldehyde and allylamine, only benzoxazine is isolated. It should be emphasized, however, that the chloro derivatives **2** and **3** are obtained with rather low yields.

Electrochemical Polymerization

All Mannich bases that we synthesized give polymer films on iron, copper, and nickel when electrooxidized in the assessed media using either the cyclic potential sweep method or the potentiostatic one.

Oxidation Potentials of Reactive Species

The oxidation potentials E_{ox} vary according to the nature of the anode metal (Fig. 2), being higher for iron compared with copper and nickel. The presence of a thin layer of oxide on the iron surface, even before polarization, explains the more difficult oxidation of phenol compounds on such metals.[22] The peculiar behavior on an iron substrate appears somewhat troublesome when discussing the influence of a Mannich base on its relative easiness of oxidation. The measured oxidation potential was not far from the free-monomer solution oxidation, being even higher in few cases (see results for **8**, **12**, and **15**). The situation for copper and nickel anodes is quite different since the measured oxidation potential can undoubtedly be ascribed to monomer oxidation (no interference with the electrolyte or metal oxidation). Thus, for copper and nickel, the relative easiness of oxidation of the Mannich bases can be determined. Both metals give the same expected results, namely, that the oxidative aptitude of Mannich bases is mostly controlled by the electronic effect of the *ortho*-aminomethyl phenol substituents. *Ortho* electron-donating groups lower the potential of oxidation, whereas electron-withdrawing groups, which stabilize the phenolate anion by

Table II Substituted *o*-Aminomethyl Phenols

$$\text{R}_1\text{—}\underset{\text{OH}}{\text{C}_6\text{H}_3}\text{—CH}_2\text{—N}\underset{\text{R}_3}{\overset{\text{R}_2}{\diagdown}}$$
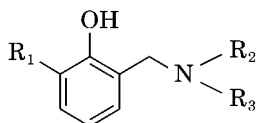
Compound[a] No.[b]	R$_1$	R$_2$	R$_3$	Condensation Method[c]	Yield[d] (%)	Boiling Point (°C/mmHg)[e]
7	H	CH$_2$—CH=CH$_2$	CH$_2$—CH=CH$_2$	A	42	70/0.8
8	H	CH$_3$	CH$_3$	A	28[a]	60/1.0[f]
9	OCH$_3$	CH$_2$—CH=CH$_2$	CH$_2$—CH=CH$_2$	A	34	97/0.7
10	OCH$_3$	CH$_3$	CH$_3$	A	29	85/0.8
11	CH$_2$—CH=CH$_2$	CH$_2$—CH=CH$_2$	CH$_2$—CH=CH$_2$	A	40	120/1.0
12	CH$_2$—CH=CH$_2$	CH$_3$	CH$_3$	A	48	90/1.5
13	H	H	CH$_2$—CH=CH$_2$	B	18	—
14	Cl	H	CH$_3$	B	—[g]	—
15	Cl	H	CH$_2$—CH=CH$_2$	B	24	—
16	CH$_3$	H	CH$_2$—CH=CH$_2$	B	47	—
17	CH$_2$—CH=CH$_2$	H	CH$_3$	B	53	—
18	H	(CH$_2$)$_2$—CH=CH$_2$	CH$_2$—CH=CH$_2$	C	42	95/1.0
19	CH$_3$	(CH$_2$)$_2$—CH=CH$_2$	CH$_2$—CH=CH$_2$	C	48	115/2.0
20	CH$_2$—CH=CH$_2$	(CH$_2$)$_2$—CH=CH$_2$	CH$_3$	C	46	105/1.0
21	CH$_2$—CH=CH$_2$	(CH$_2$)$_2$—CH=CH$_2$	CH$_2$—CH=CH$_2$	C	60	110/1.0

[a] 2,6-Bis(*N,N*-dimethylaminomethyl)phenol is also isolated in 5% yield.
[b] Note that the numbering used in all figures and discussions is as shown in these structures.
[c] See Experimental section for typical experimental procedures.
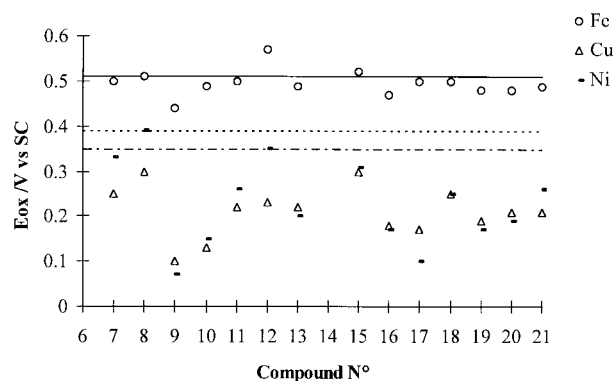[d] Yields from the starting phenols are indicated.
[e] Boiling points of Mannich bases prepared by method C are indicated even though vacuum distillation of the crude oil is not necessary.
[f] 112/20.[20]
[g] The hydrochloride does not crystallize.

charge dispersal, raise it (compare, for instance, **8**, **10**, and **12**; **7**, **9**, and **11**; **13**, **15**, and **16**; or **18**, **19**, and **21**).

Figure 2 Oxidation potentials of Mannich bases on various metal anodes (Fe, Cu, and Ni). Also referred to are the oxidation potential of the background system alone on (solid line), Fe, (- - -) Cu, and (− · −) Ni anodes.

Insulating Features

The insulating character of polymer films was investigated from the electrochemical runs, particularly giving i_{p2}/i_{p1}, i_{res}, and ΔE values (see Experimental section).

Effects of the ortho-*substituent relative to the OH group.* Figure 3 shows that the most effective films are those based on *o*-allyl and *o*-methyl phenol-type monomers. The favorable action of allylic groups on the three metals tested is ascribed to the π-electron interaction with the substrate, which causes strong adsorption of the monomer and bonding to the metal of the polymer as it is formed [Figs. 3(a–c)]. The methyl group's electron-releasing effect lowers the oxidation potential of the monomer and minimizes the occurrence of parasitic reactions (mostly electrolytic and metal oxidation). The minor contribution of the latter reaction should favor the formation of strongly insulating pure coatings. For the same reasons, the opposite effect of the *o*-chloro sub-

stituent of **15** likely explains the poor quality of the resulting coatings [Fig. 1(c,d)].

Influence of the nitrogen substituents. Figure 4 shows that *N*-methyl(s)-substituted Mannich bases give polymer films with a lower insulating character than that of *N*-allyl or *N*-but-3-enyl groups. Therefore, the basicity of the amine, favoring the formation of coordinate bonds with the metal through the unshared pair of the nitrogen atom, does not contribute at all to the quality of prepared coatings.

The electrolysis of methanolic solutions of *N,N*-dimethylbenzylamine (DMB) in the presence of KOH was found to produce methoxymethylamine (**V**) and methoxybenzylamine (**VI**) in a ratio of 4 : 1, respectively[23]:
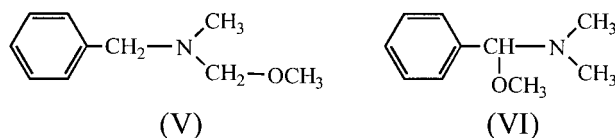

The commonly proposed pathway involves direct oxidation of the amine by an ECE route.[23,24] An indirect mechanism involving generation of methoxy radicals, which abstract hydrogen from DMB, was also proposed.[25]

In the present case, we suggest that the readily formed phenoxy radical (**VII**) is further oxidized through its nitrogen site at a potential E_2 partly determined by the electronic effect of the nitrogen substituents . $E_2 > E_1$, making allowance for the half-wave potential of 0.92 V versus SCE for DMB in acetonitrile containing 0.5M lithium perchlorate[23]:
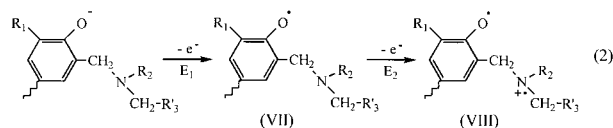
The loss of a hydrogen radical from the anodically generated cation radical (**VIII**) gives either the benzyl radical (**IX**), which spontaneously rearranges to the *ortho*-methylidene quinone (**X**) [eq. (3), path A], or the alkyl radical (**XI**), which behaves as DMB radical intermediates, that is, through solvolysis of the electro-generated cation [eq. (3), path B]:
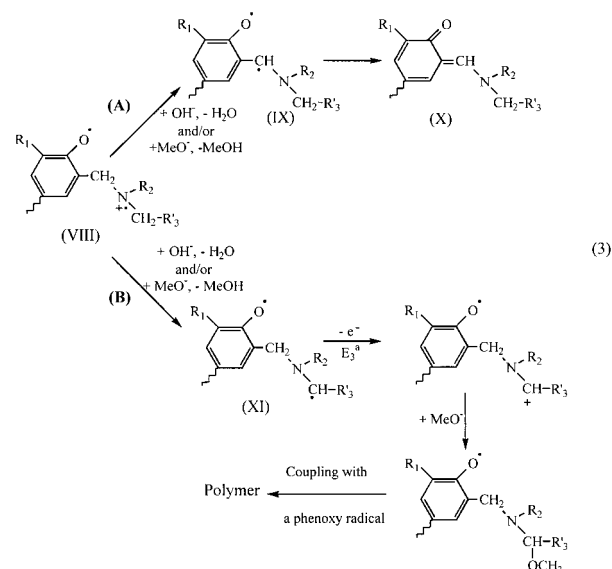

$E_3 < E_2$ (i.e., a radical is more readily oxidized than is a molecule).

It should be noted that only the direct oxidation of amine was described in eqs. (2) and (3). Radical abstraction of hydrogen from the attack of anodically generated methoxy radicals may also occur.[25] Equation (3) clearly shows that oxidation of the nitrogen of Mannich bases induces both further termination chain reactions (path A) and side reactions that do not contribute to the building of the polymer network (path B). The electron-donating of *N*-methyl(s) groups should lower the oxidation potential E_2. Therefore, the contribution of the competitive side reactions as shown in paths A and B is very likely more significant than with *N*-allyl(s) or *N*-but-3-enyl-substituted Mannich bases. Thus, the lower quality of the resulting coating can be ascribed to additional termination reactions (path A) that limit its molecular weight and, consequently, its insulating features. Furthermore, these side reactions should also lower the current yield since the thickness of the coatings does not depend on the Mannich base structure. This suggestion was further supported by the shape of potentiodynamic (Fig. 4) and potentiostatic curves (Fig. 5), both revealing higher current consumption with *N*-methyl(s)-substituted Mannich bases.

Identification of Polymer Films by IRRAS

The spectra of the polymer films obtained from **12** and **16** are shown in Figures 7 and 8, respectively. The spectra of all prepared films exhibit an intense absorption band between 1180 and

A-

B-
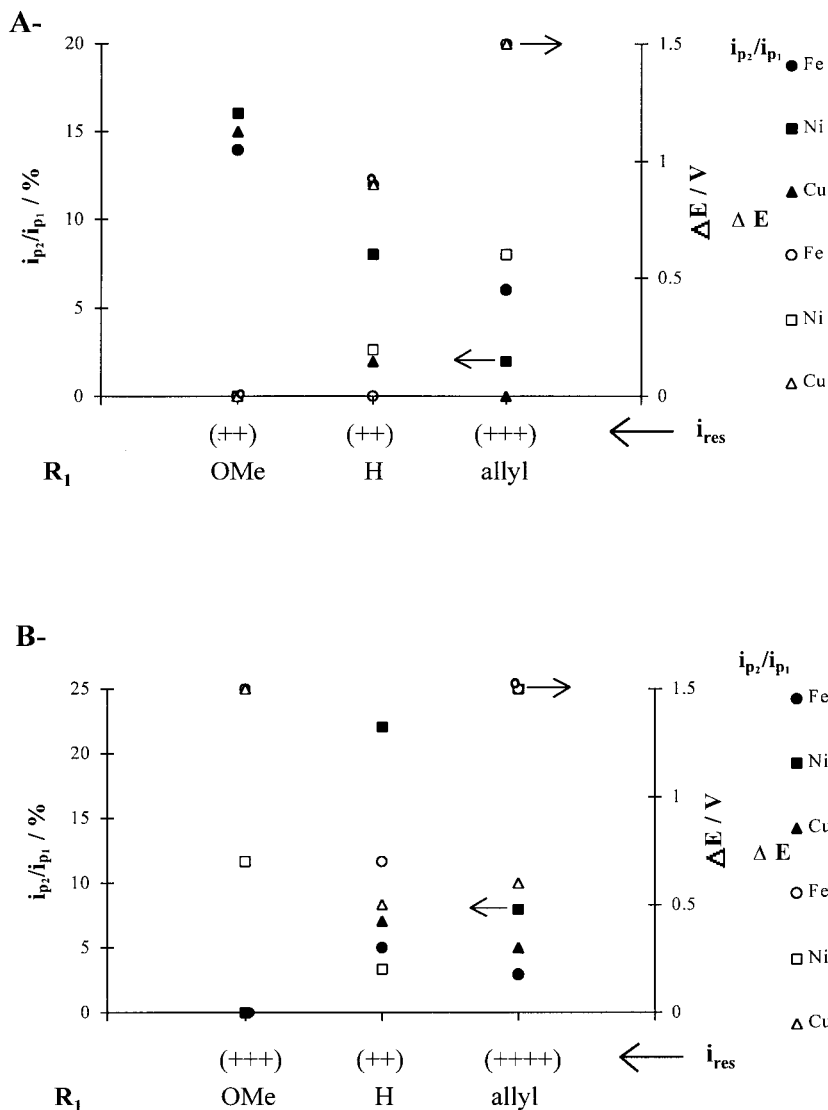
Figure 3 Dependence of film-insulating character on the *ortho* R_1 substituent (same as Table II) for (A) 2-(*N*,*N*-dimethyl)aminomethyl phenols, (B) 2-(*N*,*N*-diallyl)aminomethyl phenols, (C) 2-(*N*,*N*-allylbut-3-enyl)aminomethyl phenols, and (D) 2-(*N*-allyl)aminomethyl phenols. ΔE was arbitrarily fixed at 1.5 V whenever the measured value was higher than 1 V. For the i_{res} measure, only the most significant results on Fe are shown with $(++++) \, i_{res} < 50 \, \mu A \, cm^{-2}$, $(+++) \, 50 < i_{res} < 100 \, \mu A \, cm^{-2}$, $(++) \, 100 < i_{res} < 500 \, \mu A \, cm^{-2}$, and $(+) \, i_{res} > 500 \, \mu A \, cm^{-2}$.

1200 cm^{-1} (depending on the monomer nature) that can be attributed to the C—O—C polyoxide group usually observed with poly(phenylene oxide) films.[26] The polymer films lack the band near 760 or 740 cm^{-1} typical of the C—H out-of-plane bending vibration of three or four adjacent aromatic H atoms, respectively. The broad O—H stretching band between 2500 and 3300 cm^{-1} and the O—H deformation vibration near 1400 cm^{-1} are also absent in the polymer spectra. The broadening of the bands near 3340

cm^{-1}, referred to the N—H stretching vibration, for poly(Mannich bases) from **15** to **17** can be attributed to hydrogen bonding between macromolecular fragments. IR spectra of the poly(allyl-substituted phenols) revealed absorption bands at 1640 cm^{-1} (C=C stretching) and 985 and 912 cm^{-1} (both C—H out-of-plane deformation), all characteristic of the allylic group. This indicates that the allyl function remains unchanged during electrolysis, hence, giving crosslinkable reactive polymers.

C-

D-
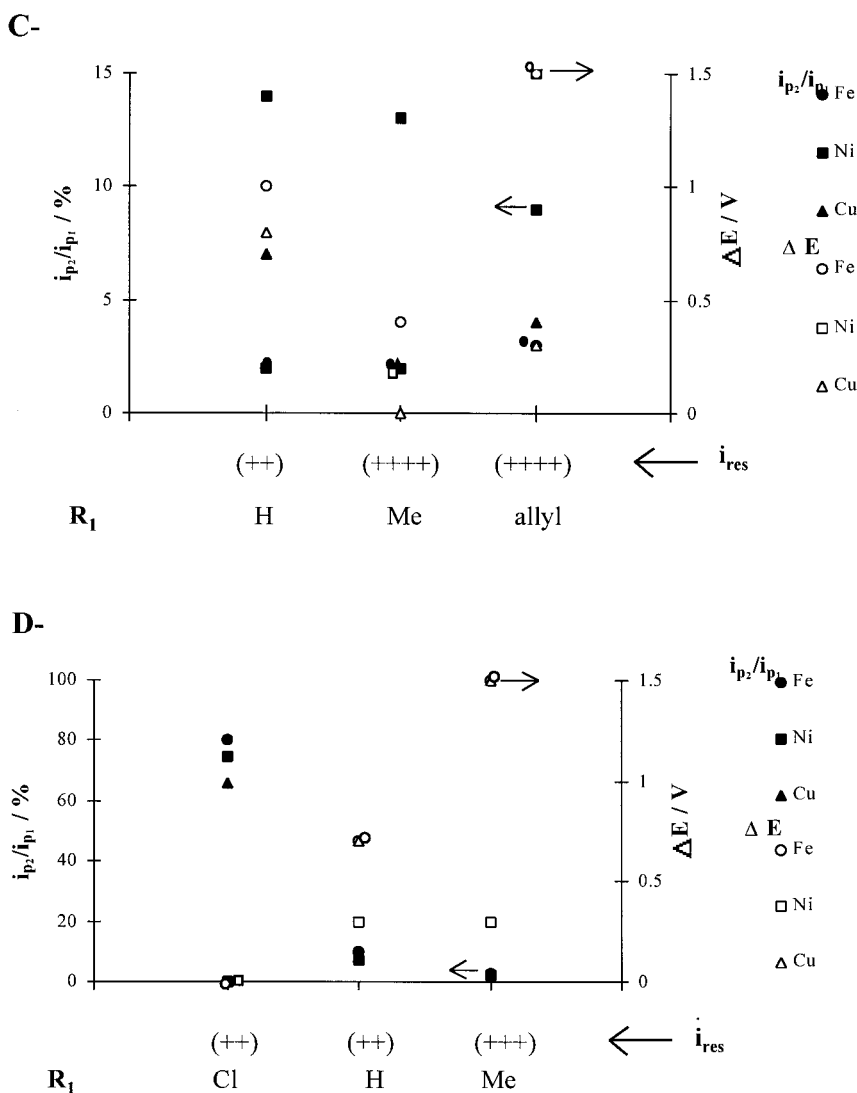
Figure 3 (*Continued from the previous page*)

The detailed IR features led to the conclusion that electrooxidation of all prepared Mannich bases occurs through head-to-tail coupling of electrogenerated phenoxy radicals as previously described, with simple phenol derivatives.[22] It should be noted that the electrooxidative mechanism for the 2,6-distributed phenols **9–12**, **15–17**, and **19–21** necessarily involves the coupling of the oxygen radical mesomer with the 4-carbon mesomer, thereby giving linear polymers. Regarding the *o*-substituted phenols **7**, **8**, **13**, and **18**, coupling in the free *ortho*-position may also occur, but IR spectra did not give evidence for it.

Therefore, polymer films with the repeating unit as shown below are obtained mainly from the investigated Mannich bases:
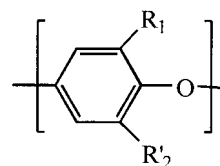
$R'_2 = CH_2NR_2R_3$; R_1, R_2, R_3 as in Table II.

Termination of electropolymerization can occur as indicated in eq. (4) [the common poly(phenylene oxide) chain termination[22]] and as in path A of eq. (3). Both reactions produce quinone-type structures hardly detectable on IR spectra as a shoulder near 1670 cm^{-1} (C=O stretching).

Properties of Coatings

The film prepared from the chloro derivative **15** showed very poor physical features (homogeneity

A-

B-

C-
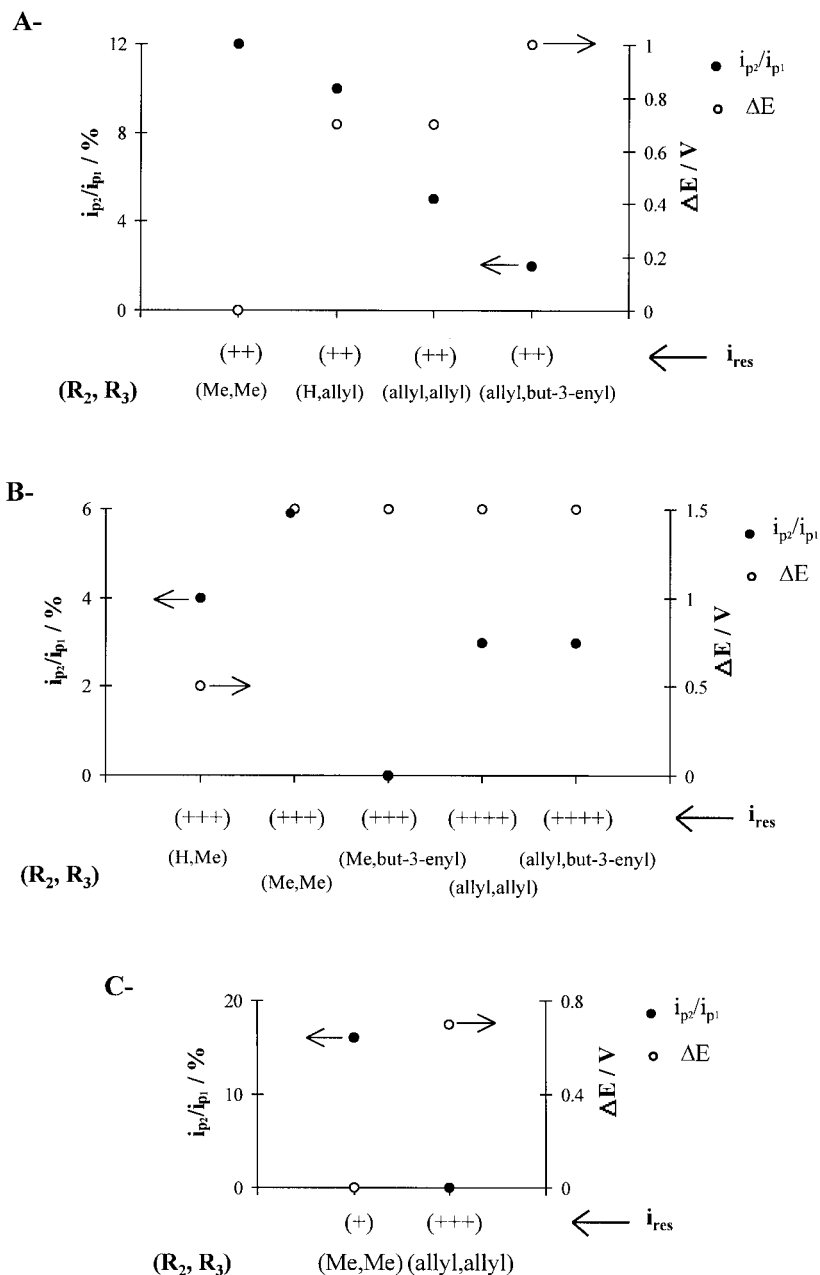
Figure 4 Dependence of film-insulating character on the nitrogen substituents R_2 and R_3 (same as Table II) for Mannich bases from various starting phenols, namely, (A) phenol, (B) 2-allylphenol, and (C) 2-methoxyphenol. Only results for the Fe substrate are indicated. Other comments as in Figure 3.

and adherence). Indeed, the barely formed film could be detached from the substrate simply during the rinsing procedure.

All coatings generated (except from **15**) are found to be poorly soluble in all the common organic solvents, thus preventing them for characterization in terms of their molecular weight. In this respect, the fraction of recovery activity of the electrode after solvent testing is only between 12

and 23% (depending on the monomer), with chloroform by far the best removal solvent.

Morphology and Thickness

Visual and microscopic examinations (scanning electron and optical microscopy) of other films reveal that a thin yellow–light brown (depending on the monomer and substrate nature) continu-
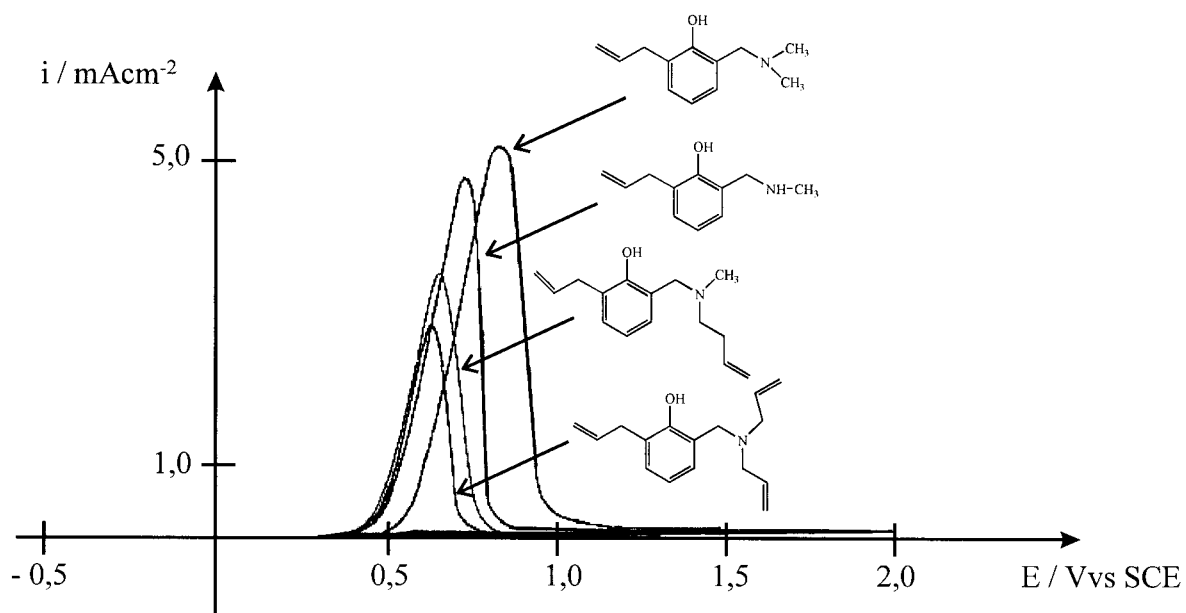
Figure 5 A comparison of voltammetric curves obtained at the iron electrode with various Mannich bases in a water–methanol (20 : 80 v/v) solution containing 0.3M KOH and 0.1M monomer (scan rate: 150 mV min^{-1}).
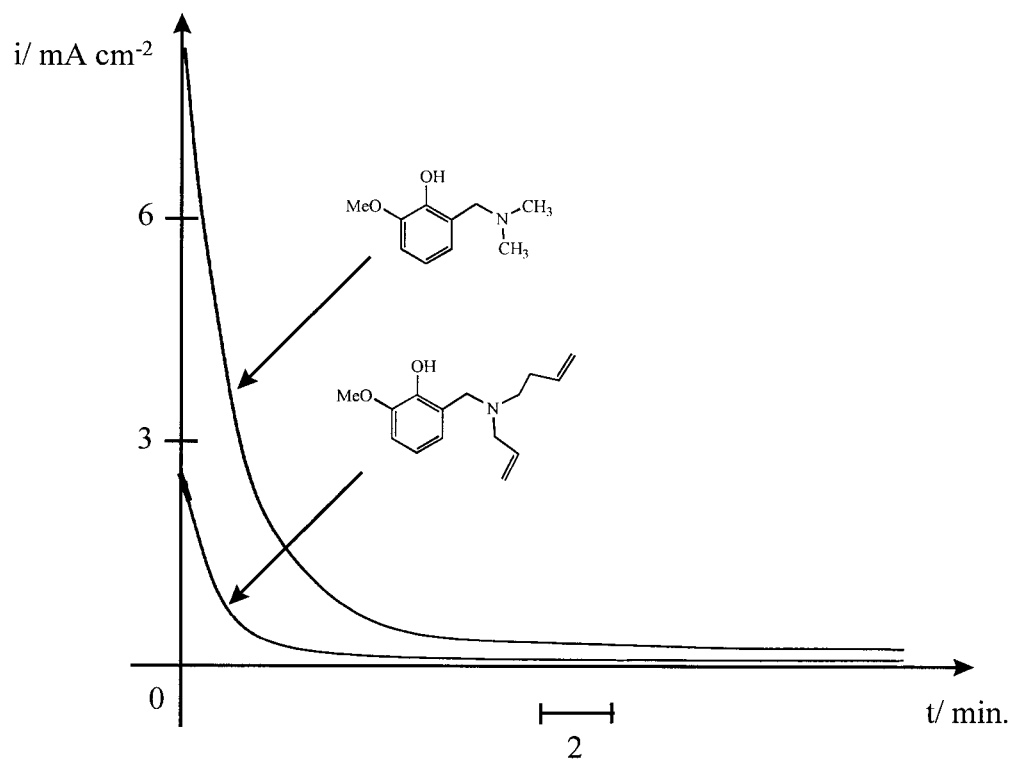
Figure 6 Comparison of current decay curves obtained at the iron electrode with various Mannich bases' electrodes in a water–methanol (20 : 80 v/v) solution containing 0.3M KOH and 0.1M monomer (applied voltage: peak potential E_p).
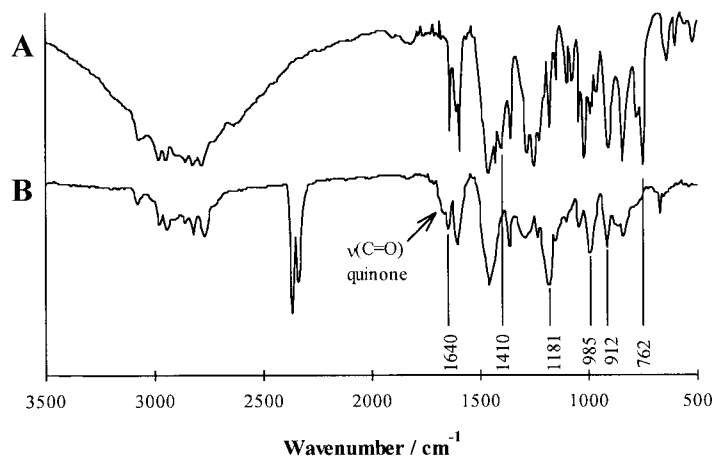
Figure 7 IR spectra of (A) 2-allyl-6-*N,N*-dimethylaminomethyl phenol (thin film) and (B) poly(2-allyl-6-*N,N*-dimethylaminomethyl phenol) (reflection–absorption spectrum).

ous coating is present on the surface, the thickness being less than 0.3 μm [Fig. 9(A)]. After additional runs with other bath compositions, the Mannich bases revealed an interesting behavior in strongly alkaline solutions with respect to the phenol compounds. The electrooxidation of a Mannich base in a free-water solution (other conditions unchanged) produces, in fact, coatings having a thickness from 2 to 5 μm, without apparent defects [Fig. 9(B)]. The hydrophilic character of the growing polymer chains (owing to the presence of amino groups) probably accounts for this result. However, the reason only free-water solutions give thick coatings is still unclear.

Adherence

All films (except from **15**) are very adherent since the activity of the electrode (estimated by measuring the peak current value when anodically cycling the coated electrode in the electrolysis bath) was still nil after peel-testing with Scotch tape.[§]

CONCLUSIONS

Polymer films on iron, copper, and nickel electrodes were prepared by electrooxidation of new and easily synthesized Mannich bases in strongly alkaline solutions. Electropolymerization using either the cyclic potential sweep method or the constant potential method gave thin, complete,

and adherent films on the three substrates, except with **15**. The poor features of the film prepared from the chloro compound was attributed to metal and electrolyte oxidation that compete with monomer oxidation. The more effective films were those based on **9**, **11**, **16**, **19**, **20**, and **21**, all substituted by allyl and/or but-3-enyl groups. The unexpected average insulating character of films from *N*-methyl(s)-substituted Mannich bases was attributed to the relative easiness of nitrogen oxidation for the latter compounds that lead to parasite reactions (methoxylation of the growing polymer chains) and to additional termination reactions.

Moreover, instead of the thin (<0.5 μm) poly(phenylene oxide) films obtained so far when a phenol derivative is electrochemically oxidized in
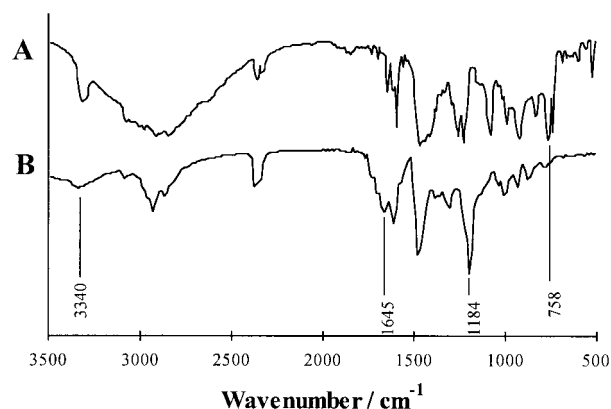
Figure 8 IR spectra of (A) 2-methyl-6-*N*-allylaminomethyl phenol (thin film) and (B) poly(2-methyl-6-*N*-allylaminomethyl phenol) (reflection–absorption spectrum).

[§] The adhesion testing procedure was fully described in an article submitted to *Corrosion Science.*
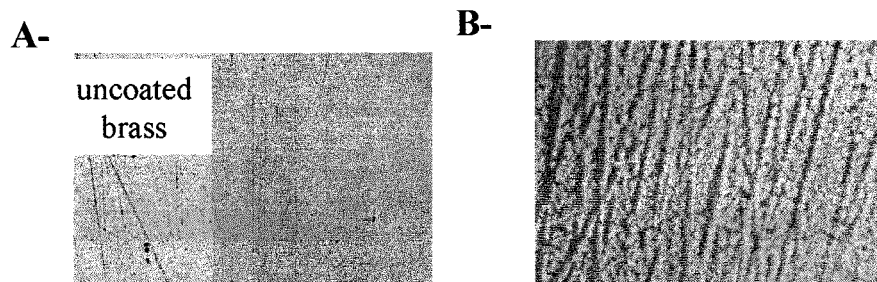
Figure 9 Photographs of the poly(2-methyl-6-*N*-allylaminomethyl phenol) on a brass electrode (G X1700). The films were formed in (A) a water–methanol (20 : 80 v/v) solution and (B) a free-water solution.

a free-additive alkaline hydroxide solution,[13] thick (>1 μm) films were prepared from Mannich bases in such free-water conditions. The amine function of the monomer was considered to increase the hydrophilic character of the growing polymer chains, thereby allowing passage of the electropolymerization current.

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