

# Poly(2-allyl)phenylene-oxide Electropolymer Film Growth on Steel

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Received 10 November 1997; accepted 15 March 2000

**ABSTRACT:** The variation of film structure and properties with growth conditions was examined for poly(2-allyl)phenylene-oxide films grown electrochemically on a mild steel substrate from a basic hydro-alcoholic monomer solution, to establish the best conditions for the production of thin, continuous, adherent films. The use of sodium hydroxide as the base led to the production of discontinuous, irregular films (upon drying). Substitution of allylamine as the base produced continuous, regular films, initially gel-like, but becoming hard and glassy upon drying or thermal treatment. Film thickness increased substantially as the pH was raised from 9.0 to 11.0, with substrate corrosion decreasing over the same range. Platinum was used as a comparable noncorroding substrate. Film thickness also increased with monomer concentration, but current flow minimized at a monomer concentration of 0.25M. Double bond functionality was retained through the polymerization process, but lost upon heat curing of the polymer films. © 2000 John Wiley & Sons, Inc. *J Appl Polym Sci* 79: 1563–1571, 2001

**Key words:** poly(2-allyl)phenylene-oxide; electropolymerization

## INTRODUCTION

Previously in this journal we have discussed the use of thin poly(2-allyl)phenylene-oxide electropolymer films as an adhesion enhancing treatment for steel blocks adhered together using polyester/styrene laminating resin.<sup>1</sup> In this report, we discuss in detail the electrochemical growth of these films, and how the film structure and properties vary with changes in the growth medium. Finally, the mechanism of heat curing within the formed polymer films is examined.

The use of the oxidative electropolymerization of phenol derivatives as a technique for producing relatively thick (>30 microns) organic coatings on

steel and other metals has been examined extensively by Mengoli and Musiani<sup>2</sup> and Mengoli et al.<sup>3</sup> Electropolymer coatings were often based on the formation of a 2-allyl phenol<sup>2</sup> or a 2-allylphenol/phenol phenylene-oxide polymer.<sup>3</sup> Allylamine and ammonia were used as base. These thick films were prepared from strongly alkaline media, often with very high potentials applied. The anticorrosion performance was described as excellent. Film formation in the presence of allylamine was examined by Kendig and Jeanjaquet,<sup>4</sup> for films grown on magnesium alloy and magnesium alloy/graphite fiber composite materials. It was concluded that in the presence of allylamine, an ionically conductive gel-like film is formed on the surface, allowing transport of the phenol derivative to the metal surface and thus continued film growth. When allylamine was not present, only thin, powdery, resistive films were formed.

The use of thin polyphenylene-oxide films as primer coatings for steel before application of a top coat, as opposed to thick protective films, has been studied by Marsh et al.<sup>5,6</sup> The presence of a

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Contract grant sponsor: Engineering and Physical Sciences Research Council (EPSRC).

*Journal of Applied Polymer Science*, Vol. 79, 1563–1571 (2001)  
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300–500-nm reactive film was found to significantly delay the onset of corrosion in alkyd-coated steel.<sup>6</sup>

In-depth discussions of the structure, chemistry, and electrochemistry of polyphenylene-oxide based polymers and electropolymers have been undertaken in our previous publications.<sup>1,7</sup>

## EXPERIMENTAL

### Specimen Preparation

Mild steel samples were prepared by mounting 1 × 1 cm squares of commercial purity mild steel, spot welded at the rear to a length of Nichrome wire, face on in polyester/styrene metallographic mounting resin with the Nichrome wire inside 6-mm plastic tubing penetrating from the rear of the specimen. This was followed by polishing using SiC disks to a "4000" grade finish.

Platinum samples were prepared as 1 × 1 cm standard flag electrodes, with both sides exposed to give a sample area of 2 cm<sup>2</sup>, except for weight gain experiments in which a 2 × 2 cm flag was used, giving an area of 8 cm<sup>2</sup>.

### Solution Preparation

Solutions were prepared by dissolving the required quantity of 2-allylphenol in 10:10:1 water/methanol/2-ethoxyethanol, a solvent found to dissolve most phenol derivatives over a wide pH range.<sup>5</sup> The solution was raised to the required pH by using sodium hydroxide or allylamine solution. The pH was measured using a HANNA-PICCOLO ATC pH meter of accuracy substantially better than 0.1 pH units (vs standard buffer solutions). It should be noted that significant (>1 mL) quantities of liquid allylamine must be used to raise the pH of 100 mL of solution above pH 10.6.

### Current-Time Transient Studies

The required solution (50 cm<sup>3</sup>) was placed in a small glass or plastic cell with a steel or platinum working electrode, a saturated calomel (SCE) reference electrode joined to the system via a solution bridge and a luggin capillary, and a platinum foil counter electrode. The working electrode was polarized to -1000 mV (SCE) for 30 s, then polarized to +1000 mV (SCE) and the current-time transient was recorded. The potentiostat used was an N. B. Thompson and Associates Ministat 251.

### Potentiodynamic Sweep Studies

The required solution (100 cm<sup>3</sup>) was placed in a glass cell with the electrodes as described previously. The potential was then swept from -1000 mV (SCE) to +2000 mV (SCE) at 50 mV/min using an ACM Instruments (Ser. 77) research potentiostat and sweep generator.

### Scanning Electron Microscopy (SEM)

These studies were performed using a Hitachi, Hitachi Amray, or ISO DS130 microscope. Where required, the internal structure and thickness of the polymer films was revealed by stressing the polymer-coated steel or platinum samples in liquid nitrogen before examination.

### Infrared Spectroscopy

Surface reflection spectra were obtained using a Perkin-Elmer Spectrum 2000 computerized Fourier transform infrared (FTIR) instrument and an adapted 2-mirror reflection cell.

### Thermally Treated Specimens

Mild steel electropolymer-coated specimens were prepared at constant potential as described previously (current-time transient studies). These were then thermally treated at 90°C overnight.

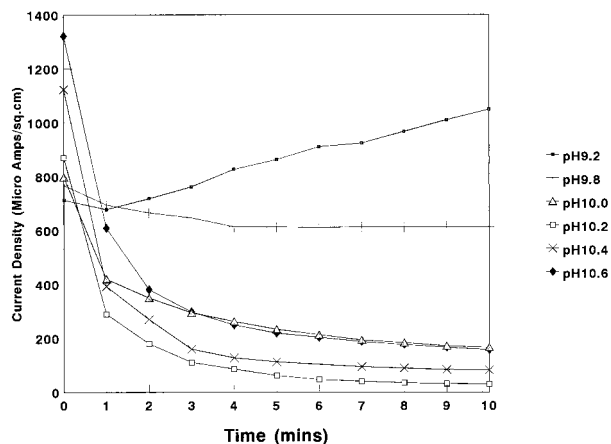
### Marker Experiments

In these experiments a platinum wire marker was placed on a horizontal mild steel electrode surface before and at various time intervals after the initiation of electropolymer film growth. The platinum wire then was examined for signs of polymer film growth using SEM.

## RESULTS

### Current-Time Transients

The first variables examined were the effect of pH and the use of allylamine as the basic agent on the growth properties of electropolymerized poly(2-allyl)phenylene-oxide films. Figure 1 shows examples of current-time transients obtained from a 0.25M solution of 2-allylphenol in the hydro-alcoholic solvent over the pH range pH 9.0–11.0, using a mild steel working electrode, allylamine base, and a polarization potential of +1000 mV (SCE). This potential lies in the region



**Figure 1** Current-time transients for a 0.25M solution of 2-allylphenol at various pH values using allylamine as the basic agent [mild steel electrode, + 1000 mV (SCE)].

of current flow suppression as determined by potentiodynamic studies, as will be discussed later.

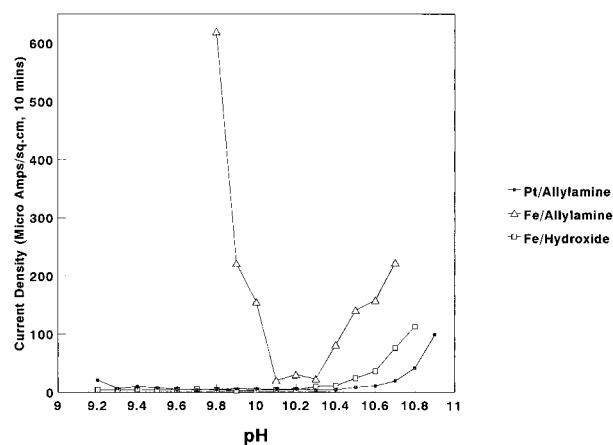
At the lower end of the pH range, the transients initially descend, then rise rapidly. Visual and microscopic examinations of the electrode surface indicated significant substrate corrosion and the formation of a thin surface film. A high current density was measured over the whole time period. As the pH rises toward 10.2, the transients descend in a smooth curve, leveling off to a constant low residual current flow after 5 to 8 min. A thin surface film can be observed on the electrode surface, with varicolored patterns visible on the electrode surface. No substrate corrosion could be observed. Above this pH, the same form of transient occurs, but the residual current flow is progressively larger with increasing pH. The films become visibly thicker with increasing pH, and assume a golden yellow color.

Attempts to relate the current-time transients to the properties of the films produced under the given conditions using a standard coulombic calculation of the area under the curve proved to be extremely difficult, because the initial current flowing was not consistent among specimens. However, one property of the transient curve was found to relate strongly to the condition of the electrode. This was the residual current flowing at the end of the transient experiment. This is a reasonable criterion to examine because the phenomena of current flow suppression are often associated with polymer formation in phenolic systems. Figure 2 shows the residual current flow at 10 min vs pH for a 0.25M solution of 2-allylphenol in the hydro-alcoholic solvent over the pH range

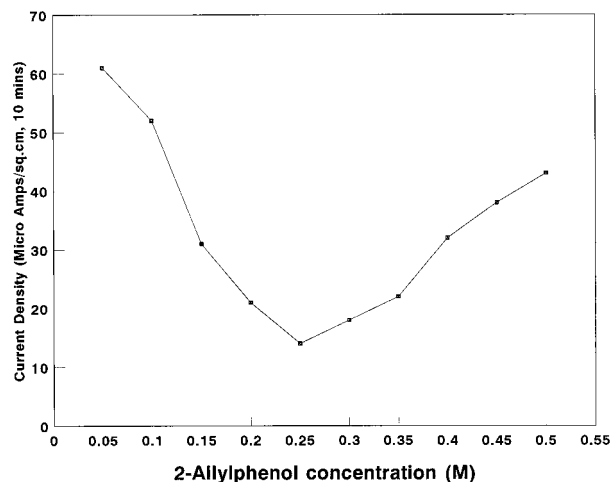
of 9.0 to 11.0, polarized to +1000 mV (SCE) for both platinum and mild steel electrodes, using alternatively allylamine and sodium hydroxide as the base.

Three zones of behavior can be noted for experiments using mild steel and allylamine, with the residual current initially descending from high values as the pH increases from pH 9.0, and can be associated with a steady decrease in the observable corrosion of the substrate. A "minimum region" then occurs at about pH 10.1, where visually thin multicolored films are produced and no substrate corrosion can be observed. Finally at pH values above 10.2 a rise in the residual current density occurs for both substrates, accompanied by an increase in film thickness (as determined both visually and using SEM). Films are initially gel-like in nature. The films become hard and glassy after drying in a vacuum desiccator for several days, presumably due to loss of residual trapped solvent, and are continuous and of regular thickness.

Examining the results obtained from a platinum working electrode under the same conditions, two major differences can be noted. First, at the lower pH end of the range, very low residual current densities are observed, as opposed to the very high current densities noted when a mild steel working electrode is used. Because we are now using a noncorroding substrate (platinum), it is clear that this effect is due to the absence of current from a substantial corrosion reaction. Second, although at the higher pH values an increase in residual current density occurs, and is accompanied by visual thickening of the surface



**Figure 2** Residual current density (current flow at 10 min) against pH for a 0.25M solution of 2-allylphenol using allylamine or sodium hydroxide as the basic agent [mild steel or Pt electrode, + 1000 mV (SCE)].



**Figure 3** Residual current density against concentration for 2-allylphenol solutions at pH 9.8 using allylamine as the basic agent [Pt electrode, + 1000 mV (SCE)].

film, both the film thickness (obtained both visually and from SEM studies) and current flows were substantially lower compared with a mild steel electrode. The rate of film growth appears to be substrate dependant.

Examining the results obtained using a mild steel electrode and sodium hydroxide as the base, again at the low pH end of the range, very low current densities are observed. No corrosion can be detected either visually or by using SEM. This clearly indicates that the severe corrosion observed when using allylamine as the base is due to the allylamine, and not the phenol derivative, and that the allylamine is in some way destroying or at least damaging any protective oxide film on the iron surface. As the residual current density begins to rise with increasing pH, the film thickness again increases, but after drying, the films produced are discontinuous and irregular, and thus of little practical use.

The next variable examined using this technique was that of monomer concentration. Solutions of 2-allylphenol were prepared as described previously, to a variety of concentrations, and the pH was raised to 9.8. A current-time transient was obtained using a platinum electrode and the residual current flow at 10 min plotted against concentration (Fig. 3). The platinum electrode was then weighed, and the weight gain was plotted against the concentration of 2-allylphenol. The use of a mild steel electrode would have been preferable, but variable solvent uptake into the mounting resin used for these specimens far out-balanced any weight gain by production of a thin

surface polymer. The equivalent film thickness was then calculated using eq. (1):

Film Thickness (microns)

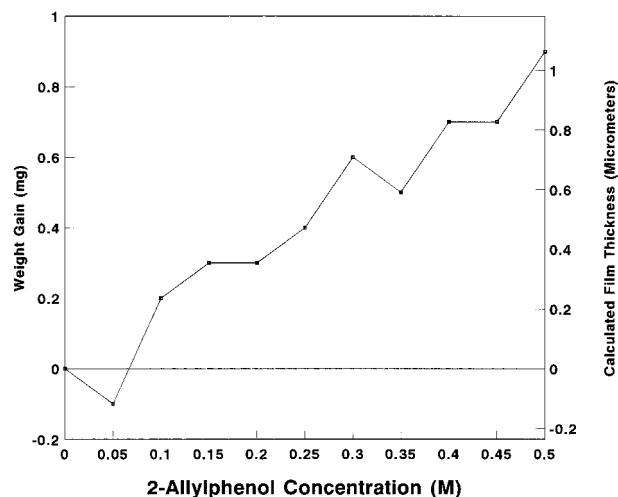
$$= \frac{\text{Weight Gain (g)} \times 10000}{\text{Density (g cm}^{-3}\text{)} \times \text{Electrode area (cm}^2\text{)}} \quad (1)$$

where density refers to chemically prepared commercial PPO ( $1.06 \text{ g cm}^{-3}$ ).<sup>8</sup>

The weight gain and equivalent film thickness results are shown in Figure 4. The best result in terms of current flow suppression occurs at 0.25M (Fig. 3). However, the calculated thickness increases roughly in proportion to the 2-allylphenol concentration. The calculated film thickness at 0.25M concentration is about 500 nm. This proves to be more than triple the thickness obtained using SEM for equivalent platinum specimens dried in a desiccator or heat cured and examined in an evacuated environment, and indicates that substantial quantities of solvent are entrapped within the gel-like films initially present on the electrode surface.

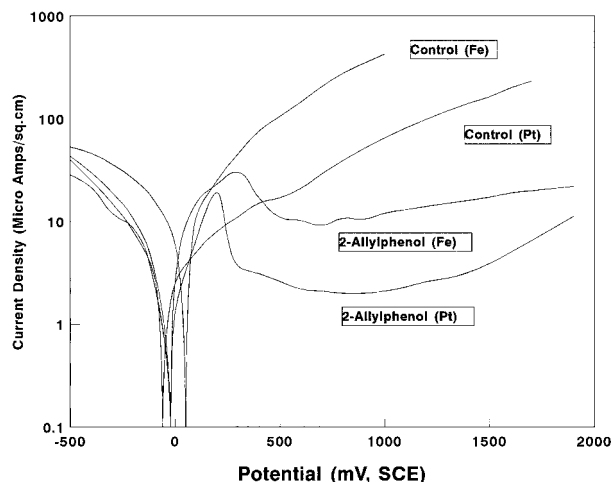
#### Marker Experiments

If a small piece of platinum wire is placed on a horizontal electrode surface before the initiation of electropolymerization, a polymer film forms on the platinum marker. If added to the surface 30 s to 1 min after the initiation of polymerization, the film forms on the substrate but not on the platinum wire. This indicates that after initiation film



**Figure 4** Weight gain and calculated film thickness vs concentration for 2-allylphenol solutions at pH 9.8 using allylamine as the basic agent [Pt electrode, + 1000 mV (SCE)].





**Figure 5** Potentiodynamic polarization curves for a 0.25M solution of 2-allylphenol of pH 10.2 using a mild steel or platinum working electrode and allylamine base.

growth occurs within the polymeric film or at the film/substrate interface, not at the interface with the solution.

#### Potentiodynamic Sweep Studies

The dynamic sweep results shown in Figure 5 were obtained from a 0.25M solution of 2-allylphenol of pH 10.2 in the hydro-alcoholic solvent (prepared as discussed previously) using a mild steel or platinum working electrode and allylamine base. The results show a surge in anodic current followed by a region of current flow suppression, a typical result described by other authors for a number of phenol derivatives on a variety of substrates.<sup>9,10</sup> It should be noted that +1000 mV (SCE) is within the suppression region. Assuming that current flow suppression is associated with film formation, this confirms the use of this potential for the current-time transients described previously.

Visual examination of the electrode surfaces after completion of the experiment showed the presence of a dark yellow surface film on both the steel and platinum working electrodes. This film was initially gel-like in nature, but became glassy and hard upon drying in a vacuum desiccator or heat curing.

#### SEM

SEM was used as described in Experimental, primarily to examine the electropolymer film thickness and nature after drying or heat curing. Fig-

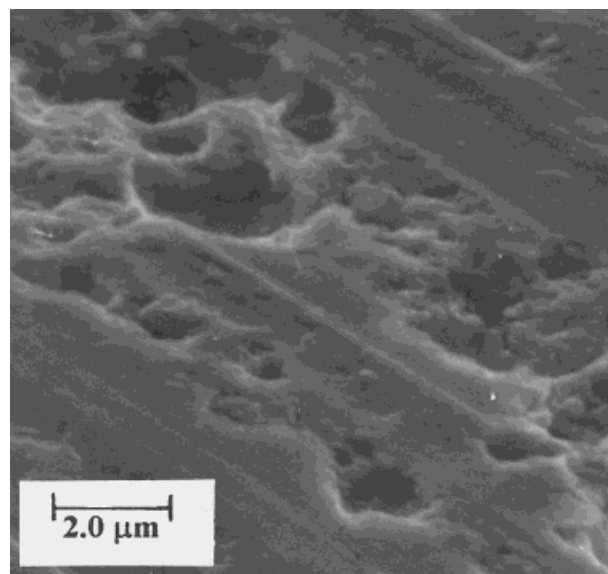
ure 6 shows a typical example of the surface of a mild steel specimen after polarization in a 0.25M 2-allylphenol/allylamine environment at pH 9.6. The corrosion of the substrate can be clearly observed. Figure 7 shows a sample prepared at pH 10.2 after fracturing in liquid nitrogen. No corrosion can be observed on unfractured specimens, and a continuous, regular film is present. Film thickness tended to be 300 to 500 nm. Figure 8 shows the film formed at pH 10.5 after fracturing in liquid nitrogen. The film is substantially thicker, and is still continuous and of regular thickness.

Replacing the allylamine base with sodium hydroxide prevented substantial substrate corrosion, but led to the production of powdery, irregular polymeric films.

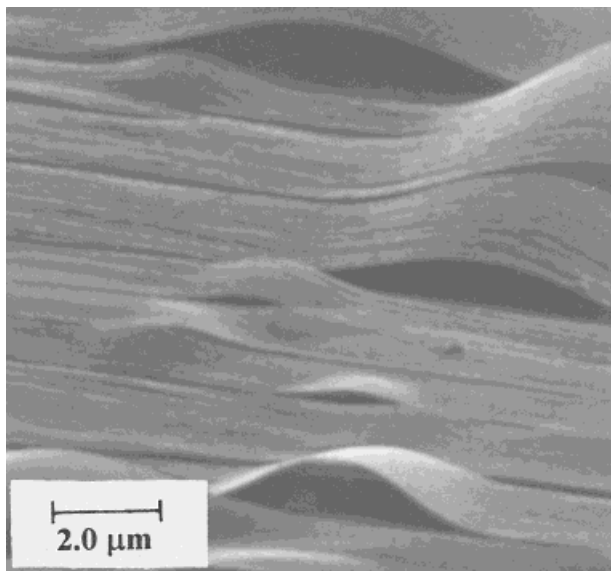
Replacing the mild steel electrode with platinum led to no substrate corrosion, and indicated that the films formed toward the alkaline end of the pH range studied were about half the thickness of those obtained on mild steel under similar conditions.

#### Infrared Spectroscopy

Figure 9 compares the FTIR spectra of a poly(2-allyl)phenylene-oxide film formed on a mild steel electrode at pH 10.2 before and after thermal treatment at 90°C overnight. The peaks associated with the presence of aromatic rings (approximate values 1450, 1485, and 1595  $\text{cm}^{-1}$ ) and



**Figure 6** SEM micrograph of a mild steel electrode after 10 min of polarization at + 1000 mV (SCE) in a 0.25M 2-allylphenol/allylamine environment at pH 9.6.



**Figure 7** SEM microcryofractograph of a poly(2-allyl)phenylene-oxide film on a mild steel electrode after 10 min of polarization in a 0.25M 2-allylphenol/allylamine environment at pH 10.2.

C—O single bonds ( $1190\text{ cm}^{-1}$ ) are clearly retained, whereas the peaks associated with the presence of an allylic double bond at about  $915$  and  $995\text{ cm}^{-1}$  are only present before heat treatment and are lost after treatment.

## DISCUSSION

The conceptual basis of this report is to convey the conditions necessary to produce thin, adherent films of poly(2-allyl)phenylene-oxide on steel, which, as discussed previously,<sup>1</sup> can be used as an adhesion enhancing treatment for a reactively compatible polymer. Also, it is important to discuss the variation in film properties with changing concentration, pH, and the presence or absence of allylamine. It is not our purpose to give a detailed mechanistic interpretation of the chemical nature of the polymerization process. This has already been undertaken in previous publications.<sup>1,7</sup> Unless stated otherwise, all comments refer to a mild steel substrate.

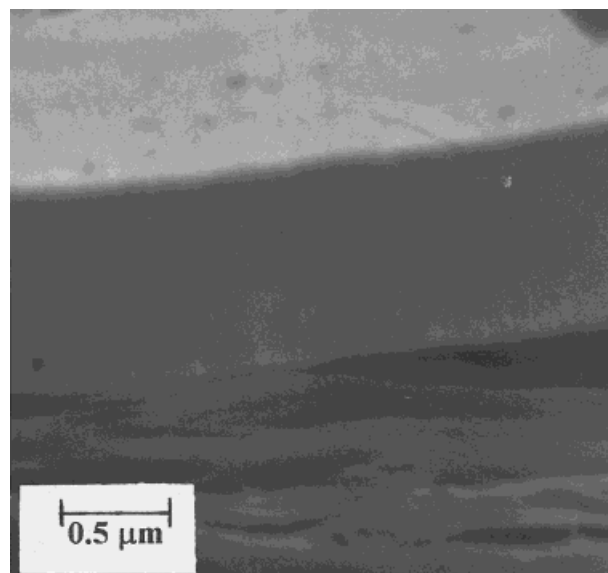
### Optimum Conditions

The optimum conditions for the preparation of thin, reactive adherent films while minimizing substrate corrosion were as follows. A 0.25M hydro-alcoholic solution of 2-allylphenol, in the pH

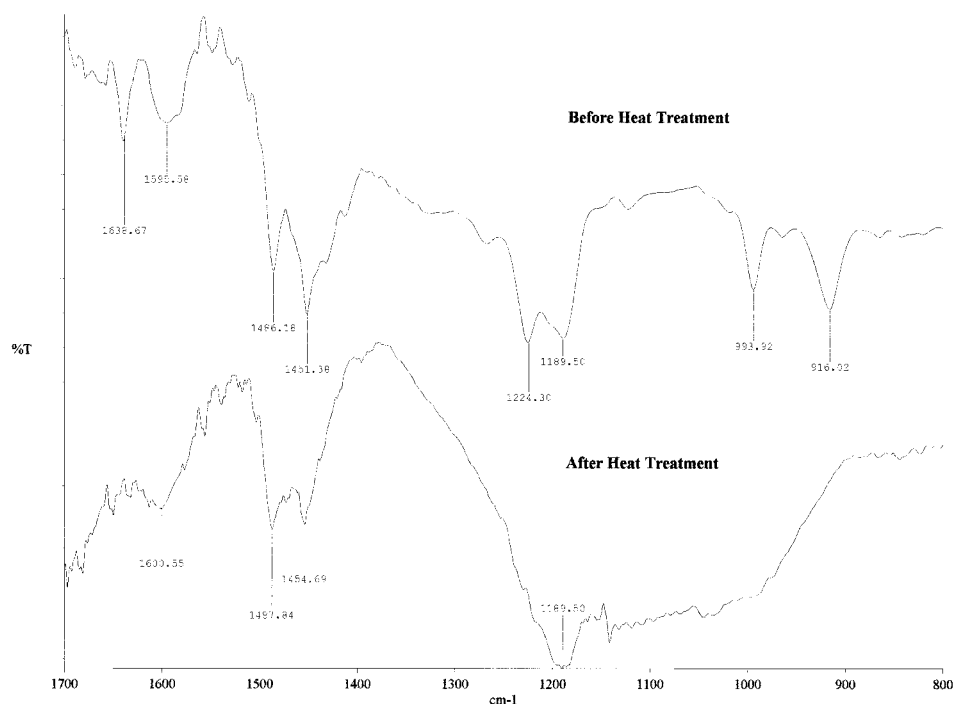
range 10.0–10.2, using allylamine as the basic agent, with a polarization potential that lies within the range of current flow suppression as established using potentiodynamic studies ( $+1000\text{ mV SCE}$  was chosen in this case, but potentials up to  $+1300\text{ mV}$  produce films that are indistinguishable). The films were initially gel-like in nature, but became hard and glassy after drying in a vacuum desiccator for several days and were 300–500-nm thick.

### Effect of Varying pH and Basic Agent

When sodium hydroxide was used as the basic agent only thin powdery films were produced, a phenomenon also noted by Kendig and Jeanjaquet.<sup>4</sup> The films were thus completely unsuitable, and an alternative agent needed to be used. Allylamine is the most well known alternative agent, having been used with respect to the formation of thick protective coatings, although other organic amines,<sup>2</sup> ammonia and ammonium salts<sup>3</sup> have also been examined. Raising the pH to the region 10.0–10.2 produced optimized films as described previously. However, if the pH was lower than this, very thin films were formed and severe corrosion of the substrate occurred (Fig. 6). Because this effect is not observed using sodium hydroxide it is clearly due to the allylamine, presumably attacking the passive surface oxide/hy-



**Figure 8** SEM microcryofractograph of a poly(2-allyl)phenylene-oxide film on a mild steel electrode after 10 min of polarization in a 0.25M 2-allylphenol/allylamine environment at pH 10.5.



**Figure 9** Surface reflective IR spectrum of an electropolymerized poly(2-allyl)phenylene-oxide film on mild steel before and after thermal treatment at 90°C overnight.

droxide film formed on iron under alkaline conditions. Electropolymerization and substrate corrosion appear to be competing oxidative reactions, with the latter decreasing as the former becomes more and more dominant. The minimum polymer film thickness that suppresses corrosion appears to be about 300 nm, so this is the minimum limit to the reactive film thickness on iron using this technique. At pH values above 10.2 even thicker films were formed (Figs. 7 and 8), mirroring the work performed by Mengoli and Musiani<sup>2</sup> and Mengoli et al.<sup>2,3</sup> who produced thick (30 micron) protective films from high fields and high allylamine concentrations. Musiani and Mengoli state that 2-allylphenol only produces “low molecular weight oils,” under the conditions used in their experiments, without thermal crosslinking or copolymerization with phenol, but Figures 7 and 8 clearly show the polymeric nature of the films formed under the conditions used in this work after drying in a vacuum desiccator.

One interesting question requiring further discussion is Why does the presence of allylamine have such a profound effect on the properties of the electropolymer film? Several possibilities have been suggested.

Musiani and Mengoli et al.<sup>2,3</sup> suggest that this and other aminos molecules attack the surface oxide film, removing or damaging any resistive

layer that could seriously effect the kinetics of polymer film growth. This is clearly indicated from the evidence presented in this publication. When allylamine is not present, and sodium hydroxide is used as a base, no substrate corrosion occurs at the lower end of the pH range examined in this publication. However, the films formed are irregular, powdery, and discontinuous. Earlier work with phenol indicated that polymer film growth often occurred at weak points in the steel surface such as scratches.<sup>5</sup> When allylamine is present, substrate corrosion can occur at the lower pH values, but at higher pH values, the polymer films formed are regular and continuous across the sample surface. In other words, these electropolymer films appear to grow poorly on a significant or undamaged oxide surface. The effect of the substrate on polymerization is examined in work conducted by Dubois et al.,<sup>9</sup> who found that for a variety of phenol derivatives on a variety of metal substrates the electropolymerization potential varied strongly with substrate. This could indicate that the nature of electropolymer film growth depends on the chemical/physical nature of the metal surface oxide.

Mengoli and Mussiani<sup>2</sup> also suggest that allylamine could act as a refining agent, acting to prevent crosslinking of the polymer and producing a straight chain, open structure. This is more

controversial and not proven, but incorporation of allylamine chemically into the polymer was clearly shown. Examination of the polymers formed in this work using X-ray photoelectron spectroscopy clearly shows the presence of a significant quantity of nitrogen within the surface layers of the polymeric structure. This nitrogen remains in the polymer even after exposure to high vacuum and thermal treatments. This indicates the presence of the amine chemically bonded into the polymeric structure.

Kendig and Jeanjaquet<sup>4</sup> convey a third suggestion. The presence of allylamine changes the nature of the growing polymer from a resistive to an ionically conductive state, enabling continued film growth to produce continuous, even films as opposed to thin discontinuous deposits. This is not unreasonable. From this work, the films are clearly initially gel-like when allylamine is present and become more gel-like with increasing allylamine concentration in the environment. This could lead to improved penetration of the monomer into the growing polymeric layer. As clearly indicated from the platinum marker experiments discussed earlier, the polymer grows from within its structure or from the polymer/metal interface, not from the interface with the solution.

We believe that, as discussed, there is evidence to suggest that all three mechanisms contribute to the polymer film growth rate and structure. Also, the results obtained in these experiments would indicate that the nature of the electrode surface and its interaction with allylamine is an important factor affecting film growth. For any given set of conditions when allylamine is present, the current flow suppression was greater for a platinum electrode, and polymer film thickness was substantially lower, when compared with a mild steel electrode. This can only be explained by a substrate surface phenomenon (perhaps preferential adsorption of species, although this is simply speculation) and not by the allylamine affecting the growth of the polymer directly as this would be independent of the substrate.

#### Effect of Varying Monomer Concentration

Examining the effect of monomer concentration using platinum flag electrodes (Figs. 3 and 4), we can see that the best performance in terms of current flow suppression occurs at a concentration of 0.25*M*. Assuming that the level of current flow suppression is related to polymer film forma-

tion and thickening, then this is the optimum concentration for the formation of thin uniform films. (In reality the situation is far more complicated. In a previous publication<sup>7</sup> we have examined the current flow suppression mechanism of a number of phenol derivatives and found that although current flow suppression does reflect the nature of the reactions taking place within the growing polymer film, it is also possible to grow films under certain conditions with no current flow suppression phenomena occurring.) At concentrations below 0.25*M* there appears to be an increasing tendency to form small soluble oxidized molecules as opposed to long chain oligomers and polymers, reducing the effective suppression of current flow. Other workers sometimes note a "concentration threshold" for polymerization. At higher concentrations, thicker films are again formed, as shown by the weight gain results and calculated film thickness. It is interesting to note that the calculated film thickness (from the electrode weight gain) of the freshly prepared films was found to be more than twice the thickness of the equivalent vacuum-dried or thermally cured films. This clearly indicates that the initial gel-like nature is due to large quantities of entrapped solvent/allylamine within the polymeric structure, possibly increasing the ionic conductivity of the electropolymer film as described by Kendig and Jeanjaquet.<sup>4</sup> The film growth process is clearly due to ionic and not electrical conductivity, as shown by platinum marker experiments. If a small piece of platinum wire is placed on a horizontal electrode surface before the initiation of electropolymerization, a polymer film forms on the platinum marker. If added to the surface 30 s to 1 min after the initiation of polymerization, the film forms on the substrate but not on the platinum wire. This indicates that after initiation, film growth occurs within the polymeric film or at the film/substrate interface, not at the interface with the solution.

#### Effect of Thermal Treatment

Thermal treatment as described previously significantly enhances the mechanical properties of the electropolymer film, increasing the film hardness and abrasion resistance. However, thermal treatment induces crosslinking of the allylic double bonds, and thus loss of the reactive functionality. Figure 9 shows the reflectance FTIR spectrum of a poly(2-allyl)phenylene-oxide electropolymer film formed on mild steel under the conditions described previously. The peaks asso-



ciated with the presence of aromatic rings (approximate values 1450, 1485, and 1595  $\text{cm}^{-1}$ ) and C—O single bonds (1190  $\text{cm}^{-1}$ ) are clearly retained, whereas the peaks associated with the presence of an allylic double bond at about 915 and 995  $\text{cm}^{-1}$  are only present before thermal treatment and are lost after treatment. Our previous article in this journal<sup>1</sup> clearly showed that the loss of the reactive allyl groups leads to a marked drop in the adhesion strength of adhesive joints formed from electropolymer-treated steel blocks when using a compatible adhesive system.

### Work by Other Authors

A final comment can be made with respect to some previous work by other authors. For example, a number of these articles examine phenol derivatives under one set of environmental pH conditions,<sup>9</sup> or with little use of microscopy to examine the electrode surface.<sup>10</sup> We believe this to be fraught with problems because we have found that even small changes in the environment, such as pH changes, can have a profound effect on both the electrochemical response and the nature of the electropolymer film. As we intend to describe in future publications, a far better understanding of the fundamental polymerization mechanisms of a number of phenol derivatives can be obtained if the conditions are varied and any changes in the electrochemical response and nature of the polymer film are then examined.

### CONCLUSIONS

Conditions have been established for the formation of thin (300–500 nm), reactive, uniform, and adherent poly(2-allyl)phenylene-oxide films on a mild steel substrate, using the electropolymerization technique. However, environmental conditions must be very carefully controlled because even small variations can lead to film thickening or severe substrate corrosion. The use of sodium hydroxide as a basic agent leads to poor quality, discontinuous films, and allylamine can be used as an alternative. When allylamine is used, film growth appears to occur from within the polymer film or at the polymer/metal interface, and not at the polymer/solution interface. Also, the rate of

film growth is substrate dependent, with higher current flows and thicker polymer films obtained on steel, as opposed to a platinum substrate.

Allylamine appears to act by damaging or dissolving the surface oxide layer on the mild steel surface, which clearly restricts polymer film growth in sodium hydroxide-based environments. It can also act by increasing the ionic and molecular conductivity of the growing polymer film, producing a gel-like *in situ* structure. There is evidence of chemical incorporation of the amine into the polymer.

Thermal treatment, used to improve the mechanical properties of the electropolymer films, cannot be used if the allyl groups are to be retained as crosslinking occurs and the functionality is destroyed.

The authors thank the Engineering and Physical Sciences Research Council (EPSRC) for providing the funding for this project, and their continuing support in this area of research.

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