

Electropolymerization of Trimethylsilylphenols to Silylated Polyphenylene Oxides and Investigation of Their Properties. Enhanced Conductivity of PPO by Silyl Group

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ABSTRACT: Polymerization of *o*-, *m*-, and *p*-trimethylsilylphenols (TMS-phenols) was achieved electrochemically. The polymers were prepared as thin films on a platinum electrode and were found to be electroinactive in nonaqueous solutions. The polymers exhibited far higher conductivities than polyphenol or other substituted polyphenols. The conductivity of poly(*p*-TMS-phenol) was lower than that observed for the polymers of the *o*- and *m*-isomers. The polymers were characterized by infrared spectroscopy. The effect of monomer concentration, supporting electrolyte concentration, current densities, and temperature on the polymerization was investigated using microgravimetry. The observed empirical kinetics were as follows. The rates of polymerization of *o*-, *m*-, and *p*-TMS-phenol were found to be of 0.8, 0.8, and 0.7 order dependent on monomer concentration, of 0.5, 0.5 and 0.45 order dependent on electrolyte concentration, and of 0.9, 0.9 and 0.8 order dependent on current densities. By investigating the effect of temperature on electropolymerization, the corresponding activation energies of electropolymerization were calculated to be 0.9, 0.9, and 0.8 kJ/mole. The molecular weights of poly(*o*-TMS-phenol) and poly(*m*-TMS-phenol) were determined by gel permeation chromatography. © 1997 John Wiley & Sons, Inc. *J Appl Polym Sci* **65**: 1121–1126, 1997

Key words: polytrimethylsilylphenols; trimethylsilylated polyphenols; electropolymerization of silyl-phenols; conducting poly-silylphenols

INTRODUCTION

Polyphenol exhibits certain unique properties such as hardness, wear resistance, and extreme thermal stability, in addition to low cost of production. It shows a wide range of conductivities depending on dopant ions.^{1–7} In general, ClO₄⁻ doped polyphenol oxide (PPO) is an insulator (conductivity < 10⁻¹⁰ S/cm). Attempts have been made, by different groups of workers, to increase the conductivity of PPO through structural changes in the monomers.⁸ Substituents such as halo,⁷ methyl,⁹ allyl,¹⁰ 2,6-dimethyl,¹¹ carboxylic,¹² and ester¹⁰ groups do not increase the conductivity of PPO to any significant extent. Even though

poly(*p*-amino-phenol) has higher conductivity (10⁻⁵ S/cm),¹³ it resembles polyaniline rather than polyphenol. In this article, we report on our observation of significant increases in the conductivity of PPO, when the monomer is substituted by trimethylsilyl (TMS) groups at different positions in the phenyl ring; the kinetics of electropolymerization; and the determination of molecular weights of *o*- and *m*-TMS-phenol polymers.

EXPERIMENTAL

A monomer-supporting electrolyte (NaClO₄) and solvent (MeOH) were purified by standard procedures. The *o*-, *m*-, and *p*-TMS-phenols were prepared from the corresponding chlorophenols. *m*-Chlorophenol was prepared from *m*-chloroaniline

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by diazotization followed by acid hydrolysis. The other two chlorophenols were readily available commercial samples. The chlorophenols were converted into their respective TMS-ethers by refluxing with TMS-Cl. A Wurtz-Fittig coupling reaction of the silyl ethers with sodium and TMS-Cl, followed by acid hydrolysis of the products in ethanol, gave the required *o*-, *m*-, and *p*-TMS-phenols with good yields.^{14,15}

The experimental set-up consisted of a Tacucel (PRT 10-0.5), France, potentiostat commanded by a Tacucel (GSTP-3), France, signal generator, and the cyclic voltammograms were recorded on a Sefram recorder (XYt), France. A three-compartment cell was used with platinum ($1 \times 1 \text{ cm}^2$), platinum ($5 \times 5 \text{ cm}^2$), and saturated calomel electrodes (SCE) as working, counter, and reference electrodes, respectively. Conductivities were measured using a homemade four-probe conductivity bridge. The current source was a homemade power source with an accuracy of $< 0.1 \mu\text{A}$. All experiments were performed at $298 \pm 1 \text{ K}$ unless otherwise specified. Polymer yield was obtained gravimetrically from the difference in weights of the Pt sample (anode) before and after the experiments. The experiments were repeated (five to seven times), and the mean values are presented with a $< 1\text{-}\mu\text{g}$ accuracy. A detailed experimental procedure on electropolymerization is discussed elsewhere.¹⁶

Gel permeation chromatographic analysis was performed with tetrahydrofuran as the eluent. Approximately 0.05% solutions of the films were made. A 20-mL sample was then injected into a Hewlett Packard HP 1090 liquid chromatograph which utilized a microstyrigel column with a porosity of 1,000 Å. Adequate sensitivity was obtained with the 254-nm detector, and the elution rate was 0.8 mL/min. The void volume (V_o) was determined using a very high-molecular-weight polystyrene standard (8.5×10^6). Calibration curves of logarithm molecular weight against relative elution volume (V_e/V_o) of monodisperse polystyrene standards of known molecular weights showed a linear range from 22,000 to 3,250. The molecular weight of the polymer was deduced from the standard curve. Infrared (IR) measurements were made by using KBr pellets of the polymers on a BOMEM MB-100 Fourier transform IR instrument.

RESULTS AND DISCUSSION

Polymerization

A typical voltammogram recorded in MeOH containing 0.1 mM *o*-TMS-phenol and 0.1M NaClO₄

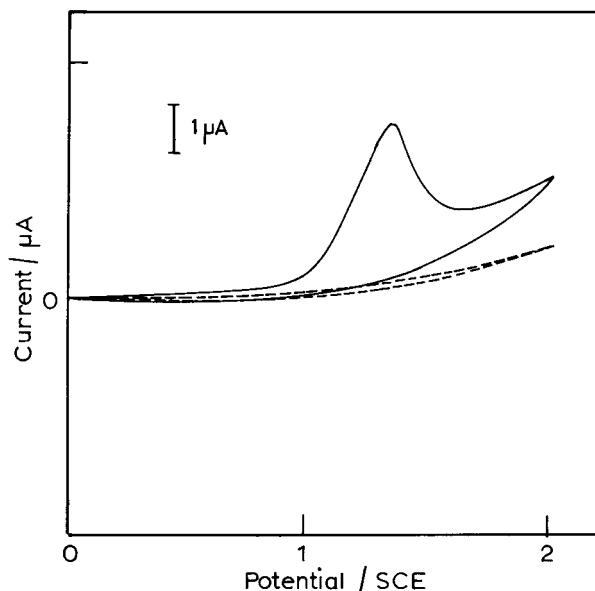


Figure 1 Voltammogram of 0.1 mM *o*-TMS-phenol and 0.1M NaClO₄ in methanol.

is shown in Figure 1. In the first forward scan, an anodic peak was observed at 1.18 V versus SCE. This peak is considered to correspond to the electrochemical oxidation of phenols.^{17,18} During the reverse scan, no cathodic peak was observed, indicating the irreversible oxidation. As the potential scan was continued, the anodic peak decreased gradually. This was coupled with the formation of a yellow film on the platinum electrode. The thickness of the film increased with the amount of charge passed. On repeated cycling, a dark brown film was found to coat the electrode. The same film was also obtained galvanostatically at 5 mA cm^{-2} . Films with thicknesses of approximately $100 \mu\text{M}$ (galvanostatically) were produced depending on the amount of charge passed. Good quality films could be obtained, for instance, by applying 5 mA cm^{-2} for 30 min ($30 \mu\text{M}$). Similar results were obtained for *m*- and *p*-TMS-phenols, except that the anodic peak potential was slightly altered.

The films were found to be electroinactive when cycled in the monomer-free electrolyte, indicating that the film is stable toward both oxidation and reduction. The polymers are thermally stable and do not melt up to 260°C . Poly(*o*- and *m*-TMS-phenols) were soluble in acetone, ether, and tetrahydrofuran (THF), while poly(*p*-TMS-phenol) is sparingly soluble in these solvents.

IR Spectral Analysis

The IR spectral data of *o*-, *m*-, and *p*-TMS-phenols and of the films formed from their electro-oxida-

Table I IR Absorption Spectra of *o*-, *m*-, and *p*-TMS-Phenols and Their Polymers

Compound	Vibration Mode (frequencies in cm ⁻¹)					
	$\nu(\text{O—H})^a$	$\nu(\text{C—H})^b$	$\nu(\text{C=C})^c$	$\delta(\text{C—H})^d$	$\nu(\text{C—O—C})^e$	$\nu(\text{R}_3\text{Si—Ph})^f$
<i>o</i> -TMS-phenol	3,520	2,960	1,599, 1,500, 1,473	750		1,130, 850
<i>o</i> -TMS-phenol polymer		3,063	1,627, 1,570, 1,475	750, 870, 963	1,206	1,120, 828
<i>m</i> -TMS-phenol	3,316	2,950	1,575, 1,485, 1,425	753		1,110, 834
<i>m</i> -TMS-phenol polymer		2,937	1,640, 1,470, 750	750, 876, 963	1,253	1,121, 841
<i>p</i> -TMS-phenol	3,500	2,960	1,575, 1,485, 1,450	760		1,110, 840
<i>p</i> -TMS-phenol polymer		3,063	1,600, 1,491, 1,460	745, 876, 963	1,235	1,121, 840

^a Stretching vibration of O—H bonds.

^b Stretching vibration of C—C and C—H bonds of benzene nuclei.

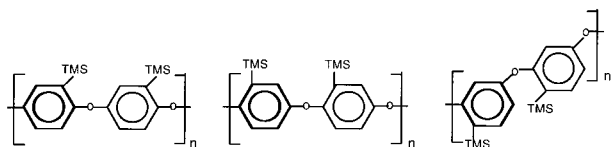
^c Stretching vibration of C=C.

^d Bending vibration of C—H bonds.

^e Stretching vibration of C—O—C bonds.

^f Stretching vibration of alkyl Si—Ph bonds.

tion are summarized in Table 1. The absorption peaks at 2,937–3,063 and 1,425–1,600 cm⁻¹ are characteristic of the stretching vibration modes of the C—H and C=C bonds of the aromatic nuclei.^{19,20} The peaks at 1,110–1,130 cm⁻¹ and at 827–841 cm⁻¹ are due to the stretching vibration of alkyl Si—Ph and SiMe₃ groups²¹ and are observed in both the monomers and the polymers, indicating the presence of an Me₃Si group. The significant change in the IR spectra of the polymers as compared with those of the monomers is the disappearance of the characteristic stretching vibration of the free O—H group at 3,252–3,316 cm⁻¹. The appearance of peaks at 1,206–1,253 cm⁻¹, characteristic of the C—O—C bond in the polymers, confirms the presence of this linkage. The peaks at 745 and 963 cm⁻¹ are considered to correspond to 1,2-disubstituted, 1,2,3-trisubstituted, and 1,2,4-trisubstituted benzene structures.²² In light of earlier reports on the anodic oxidation of phenols^{23–26} and on the basis of our observation, we propose the following structures for the polymers:



Polymers obtained by the electro-oxidation of *o*-, *m*-, and *p*-TMS-phenols were found to be of much higher conductivity compared with the conductivities reported for polyphenol or polyphenols

with substituents like chloro, bromo, methyl, 2,6-dimethyl, allyl, carboxylic, and ester groups (Table II). Thus, the TMS group, especially in the *o*- and *m*- positions, seems to be very effective in bringing about a sharp increase in the conductivity of the TMS-phenol polymers.

Effect of Various Parameters on Polymerization

Effect of Monomer Concentrations

Figure 2(A) depicts the effect of the monomer concentration on the kinetics of polymerization. The polymerization was found to be linear with monomer concentration for the given experimen-

Table II Effect of Substituents on the Conductivity of PPO

Substituents	Conductivity ^a (S/cm)	References
Halo	10 ⁻¹⁰	7
Me	10 ⁻⁷	9
Allyl	<10 ⁻¹⁰	10
2,6-di-Me	10 ⁻⁸	11
COOH	10 ⁻¹⁰	12
COOR	10 ⁻¹⁰	10
NH ₂	10 ⁻⁵	13
<i>o</i> -TMS	10 ⁻³	— ^b
<i>m</i> -TMS	10 ⁻⁴	— ^b
<i>p</i> -TMS	10 ⁻⁷	— ^b

^a With ClO₄⁻ as dopant ion.

^b This study.

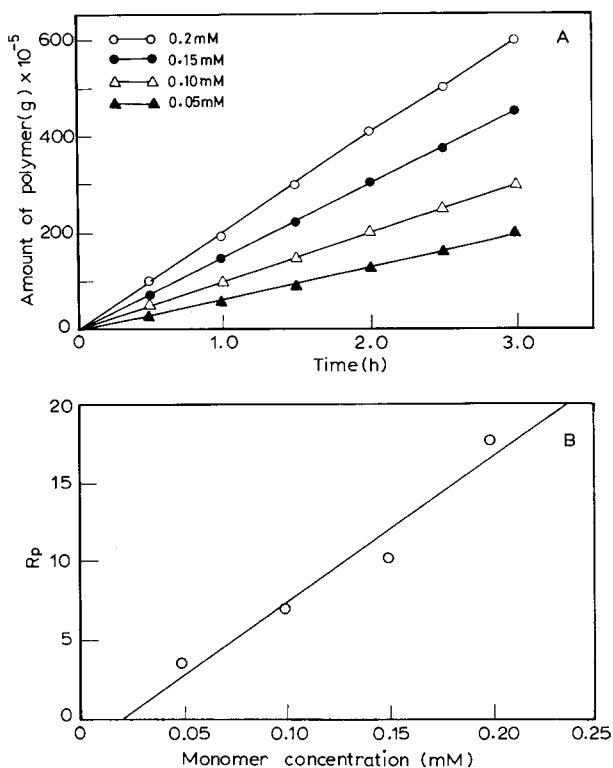


Figure 2 (A) Polymer weight obtained at different polymerization times and different monomer concentrations. (B) Dependence of R_p on monomer concentration during electropolymerization of *o*-TMS-phenol.

tal condition. Each straight line in this figure represents the variation in polymer weight generated on the electrode by electrochemical oxidative polymerization in a 1.0M NaClO_4 solution in methanol and at the correlative monomeric concentrations. The monomer concentrations selected for the study were 0.2, 0.15, 0.1, and 0.05 mM. For each concentration, the amount of polymer formed at intervals of 30 min was measured over a period of 3 h. Plotting of the amount of polymer versus time gave six points in each case, which formed a well-defined straight line. The polymerization rate (R_p) was calculated from the slope for each concentration. An increase in the polymerization rate (the slope) was observed when the monomer concentration was increased. The reaction order was obtained by plotting the logarithm of R_p versus the logarithm of the monomer concentration. Figure 2(B) shows the results obtained indicating a reaction order of 0.8 for the formation of poly(*o*- and *m*-TMS-phenols). Under identical experimental conditions, the kinetics of the electropolymerization of *p*-TMS-phenol at different monomer concentrations were also investigated. The kinetics profile was found to be similar to that

observed for the *o*- and *m*-isomers. However, a reaction order of 0.7 dependent on monomer (*p*-TMS-phenol) concentration was found.

Effect of Electrolyte Concentration

The same experimental procedure was followed, keeping the monomer concentration constant (0.2 mM) at different electrolyte concentrations: 1.0, 0.5, 0.25, or 0.12 M. Figure 3 presents the results of electrolyte concentration on the kinetics of the electropolymerization of *o*-TMS-phenol. The increase in the polymerization rate with the increase in the electrolyte concentration (NaClO_4) could be either due to the increase in the conductivity of the medium or due to the faster oxidation of the polymer film generated.²⁷ The reaction orders for *o*-, *m*-, and *p*-TMS-phenols were calculated to be 0.5, 0.5, and 0.45, respectively, dependent on electrolyte concentration.

Effect of Current Densities

The influence of current densities on the polymer generation at constant monomer and electrolyte

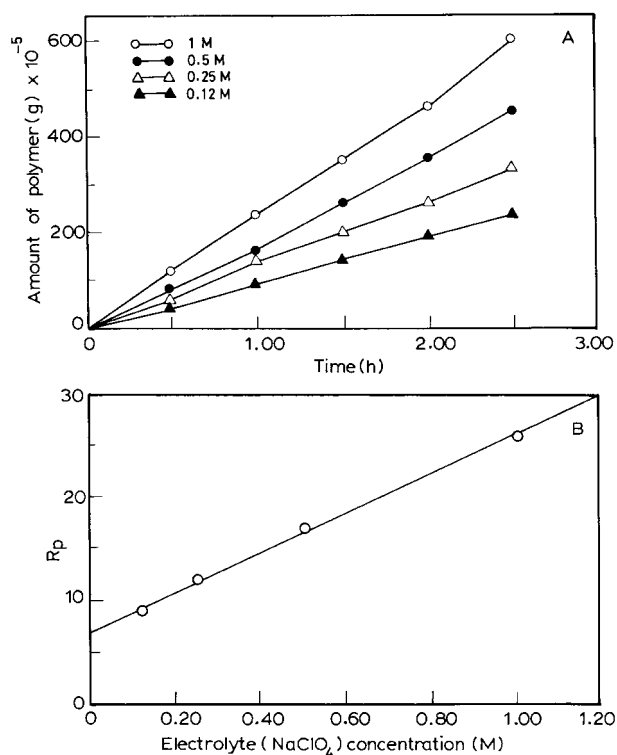


Figure 3 (A) Polymer weight obtained at different polymerization times and different electrolyte concentration at constant monomer concentration (0.2 mM). (B) Dependence of R_p on electrolyte concentration during electropolymerization of *o*-TMS-phenol.

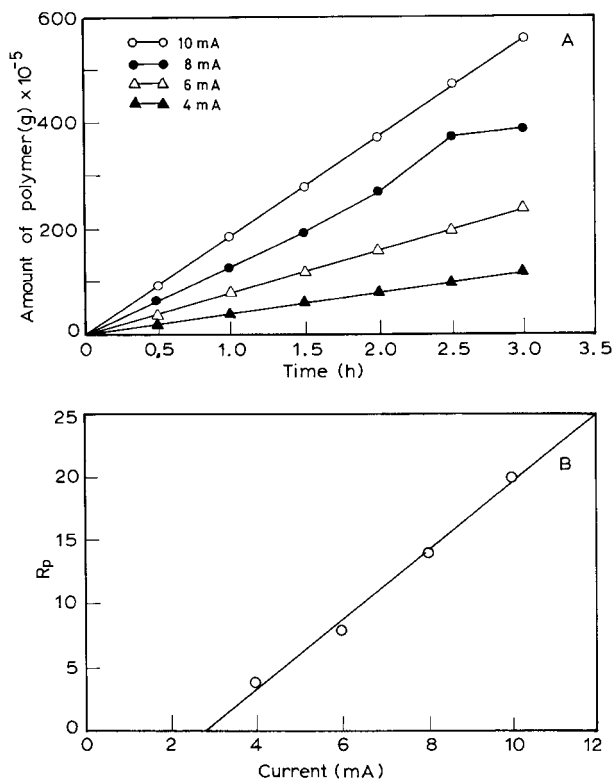


Figure 4 (A) Polymer weight obtained at different current densities and at different times at constant monomer concentration (0.2 mM) and constant electrolyte concentration (1.0M). (B) Dependence of R_p on current densities during electropolymerization of *o*-TMS-phenol.

concentrations (0.2 mM and 1.0M) was also investigated. A linear dependence on current was observed. Figure 4 shows the kinetics of the polymerization of *o*-TMS-phenol at different current densities. The effect of current density on the electropolymerization of *m*- and *p*-TMS-phenols was investigated under similar experimental conditions. From these results, the rates of polymerization were found to be of 0.9, 0.9, and 0.8 order dependent on current density for *o*-, *m*-, and *p*-TMS-phenols, respectively.

Effect of Temperature

Results of an investigation of the influence of temperature on the kinetics of the electropolymerization of *o*-TMS-phenol at constant monomer and electrolyte concentration (0.2 mM and 1.0M) with a constant current density of 10 mA are summarized in Figure 5. Using values of the rate of polymerization, an Arrhenius plot was constructed by plotting a double logarithm of R_p versus $1/T$. A similar investigation was done on *m*- and *p*-TMS-

phenols. The activation energies for electropolymerization for the *o*-, *m*-, and *p*-TMS-phenols were found to be 0.90, 0.90, and 0.80 kJ/mol, respectively.

Molecular Weight of *o*- and *m*-TMS-Phenol Polymers

The molecular-weight profiles of polymeric films obtained from the electropolymerization of *o*- and *m*-TMS-phenols were determined by gel permeation chromatography. The results are presented in Figure 6. It is observed that poly(*m*-TMS-phenol) is more homogeneous than poly(*o*-TMS-phenol). Since the poly(*p*-TMS-phenol) was sparingly soluble in tetrahydrofuran, its molecular weight profile could not be evaluated.

CONCLUSIONS

The conductivity of PPO can be greatly increased by introducing TMS groups at appropriate posi-

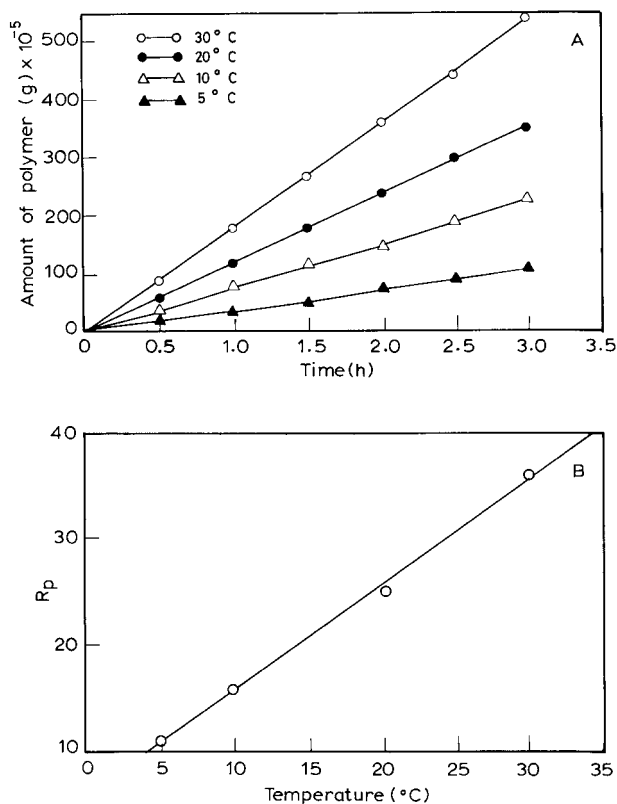


Figure 5 (A) Polymer weight obtained at different temperature and at different times at constant monomer concentration (0.2 mM), electrolyte concentration (1.0M), and current densities (10 mA). (B) Dependence of R_p on temperature during electropolymerization of *o*-TMS-phenol.

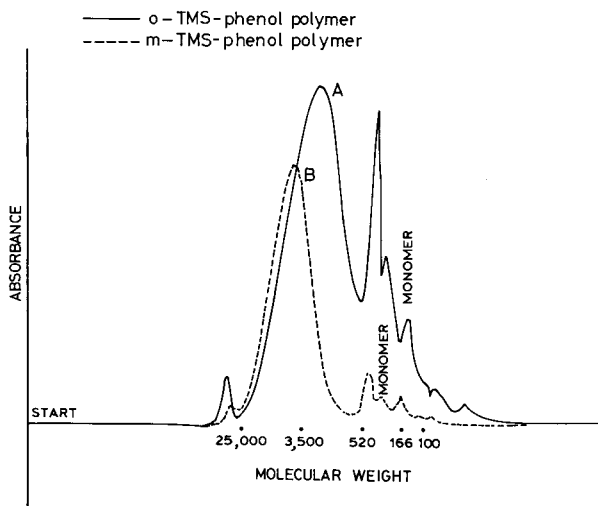


Figure 6 (A) HPGPC chromatogram for the poly(*o*-TMS-phenol). (B) High performance gel permeation chromatography (HPGPC) chromatogram for the poly(*m*-TMS-phenol).

tions in the phenol ring. The lower conductivity of poly(*p*-TMS-phenol) compared with that of poly(*o*-TMS-phenol) or poly(*m*-TMS-phenol) indicates that its structure is probably reticulated. In the absence of knowledge of the overall mechanism of electropolymerization, an empirical model of interfacial reactions would support *a priori* control of the physical properties when conducting polymer films are electrogenerated.

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