

SYNTHESIS OF SOLUBLE POLY(3,4-DIHYDROXY-*o*-TOLYLENE): REDOX POLYMER

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Abstract Conventional chloromethylation, paraformaldehyde/hydrogen chloride in acetic acid medium, was applied to 1,2-dimethoxybenzene. Chloroform-soluble poly(3,4-dimethoxy-*o*-tolylene) was obtained with an intrinsic viscosity of 0.034 dL g⁻¹. The polymer was evaluated as a condensation redox polymer precursor formed by a Friedel-Crafts reaction. Cleavage of the methoxy groups present in this polymer resulted in poly(3,4-dihydroxy-*o*-tolylene) which manifested a great air-oxidation resistance. The redox property of the latter polymer was found to be 1017 mV by potentiometric titration with 0.05 N ceric ammonium nitrate at 25°C. This midpotential was compared to that of catechol, a monomeric analogue, under the same titration conditions.

Keywords: Poly(3,4-dimethoxy-*o*-tolylene); Poly(3,4-dihydroxy-*o*-tolylene); Redox polymer.

INTRODUCTION

Of the many reactive polymers, redox polymers have gained a special interest throughout the years^[1, 2]. This is because the redox polymers exhibited peculiar properties that made them appropriate materials such as sensors, electrode coatings, antioxidants, catalysts for electrochemical reactions, electrical conductors, corrosion and degradation inhibitors^[3] in many applications. Though this interest started so many years ago, research is still devoted on this subject. Hydroquinone and catechol-containing polymers are among the most studied redox polymers. Their preparation has been extensively studied^[1, 2].

Ober *et al.* prepared polyvinylhydroquinone with a polydispersity index of 1.5 using the recent method of polymerization "stable free radical polymerization" (SFRP)^[4] and their redox property was ascertained by using cyclic voltammetry. Hydroquinone and catechol units were chemically anchored onto polyacrylic acid through an oxidative decarboxylation^[5] and their redox property was revealed by its midpotential which was determined by potentiometric titration.

This work deals with the synthesis of soluble poly(3,4-dihydroxy-*o*-tolylene), a poly(*ortho*-tolylene) (POT) derivative, through its dimethylated precursor. The thermal and solubility properties of this precursor and the redox properties of its dihydroxy analogue are outlined.

EXPERIMENTAL

Materials and Measurements

The chemicals were purchased from Fluka AG and Aldrich (France) and solvents were distilled before use. Catechol was used without further purification.

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The gas chromatography analysis was performed on a Shimadzu–Gas Chromatograph (GC-14B) with SE30 as the stationary phase.

The melting points were measured using a Melting Point Apparatus SMP3.

The viscometric measurement of polymers was performed in chloroform at 25°C with a Cannon Ubbelohde capillary viscometer 532 10/I, Schott-Gerate CT 1650. The average-viscosity molecular weights M_v were estimated by the relation of Mark-Houwink-Sakurada equation, $[\eta] = KM_v^a$, where $[\eta]$ is the intrinsic viscosity; K and a , the Mark-Houwink constants, are taken as $7.6 \times 10^{-5} \text{ dL} \cdot \text{g}^{-1}$ and 0.76, respectively^[6]. Infrared spectra were recorded with a Genesis II FT-IR spectrometer. KBr pellets were used for solid samples and Nujol for resinous samples.

Differential scanning calorimetry thermogram was recorded on Setaram Labsys DSC 16 instrument at a heating rate of 5 K/min under nitrogen atmosphere.

Potentiometric titrations were conducted under nitrogen atmosphere using a platinum working electrode and a calomel reference electrode coupled to a Digital Multimeter Tech 6150 DM. The potential was calculated as $E = E_r + E_c$, where E_r is the reading potential against the calomel reference and E_c is the potential of the calomel against the hydrogen electrode; E_c is taken as 244 mV for 25°C^[7].

Synthesis of 1,2-Dimethoxybenzene

In a 250 mL round bottom three-necked flask equipped with a thermometer, a magnetic stirrer and a condenser, 11 g (0.1 mol) of catechol were charged and dissolved in 100 mL of 2 N sodium hydroxide aqueous solution. An amount of 26 g (0.2 mol) of dimethylsulfate in three portions was added. Upon addition of the first portion to the mixture while being vigorously stirred, a rise in temperature was noted, indicating an exothermic reaction. The two remaining portions were added to the mixture at 5 min intervals. After the temperature dropped, the system was heated for 30 min at 40°C under stirring. Then, the mixture was cooled to room temperature, and the product was extracted with diethyl ether. The ethereal extract was washed twice with 5% aqueous sodium bicarbonate, and finally with distilled water. The ethereal layer was dried over anhydrous magnesium sulfate for 24 h. The liquid product was isolated by evaporation of ether (12.98 g, 89%). This liquid crystallized at 22°C which was identified as 1,2-dimethoxybenzene (veratrole) by gas chromatography analysis using a commercial veratrole as a reference standard. The liquid product was purified by recrystallization in diethyl ether (m.p. 22°C).

Synthesis of Poly(3,4-dimethoxy-*o*-tolylene)

In a 250 mL round bottom three-necked flask equipped with a thermometer, a magnetic stirrer and a condenser, 1.5 g (0.05 mole) of paraformaldehyde were charged and dissolved in 20 mL of concentrated hydrochloric acid. To this solution, 180 mL of acetic acid were added and hydrogen chloride gas was bubbled into the above solution while being vigorously stirred. As soon as the system became homogeneous, 5 g (0.036 mol) of 1,2-dimethoxybenzene were introduced. The reaction system was stirred for 1 h at 65°C. After this reaction time, a white product precipitated from the medium and was then isolated by filtration. This precipitate was washed with methanol and dried in an oven for two days at 40°C. The weight of the dried product was 1.12 g. The filtrate was washed several times with 5% aqueous sodium carbonate until a neutral pH. Diethyl ether was added to the filtrate to extract organic products. The ethereal extract was washed with distilled water and dried over anhydrous magnesium sulfate. A semi-solid tacky product resulted after evaporation of ether was 5.88 g.

Demethylation of Poly(3,4-dimethoxy-*o*-tolylene)

In a 250 mL round bottom three-necked flask fitted with a thermometer, a condenser and a magnetic stirrer, 0.5 g of poly(3,4-dimethoxy-*o*-tolylene) was mixed with 30 mL of acetic acid. While being stirred, the mixture was refluxed for 2 days at 30°C until dissolution of the polymer. The mixture was then heated at 70–80°C under nitrogen atmosphere followed by a dropwise addition of 20 mL of 48% hydrobromic acid into the solution. Afterwards, the system was heated at 120°C for 2 h under stirring and nitrogen atmosphere. After cooling the system to room temperature, the mixture was poured into 500 mL of ice-water, and the product precipitated. The latter product was filtered under nitrogen atmosphere to exclude the possible air-oxidation. The wet product was

readily soluble in methanol and insoluble in chloroform. The product was washed with chloroform. After drying at 40°C in oven for 2 days it gives a greenish product weighing 0.28 g.

Potentiometric Titration

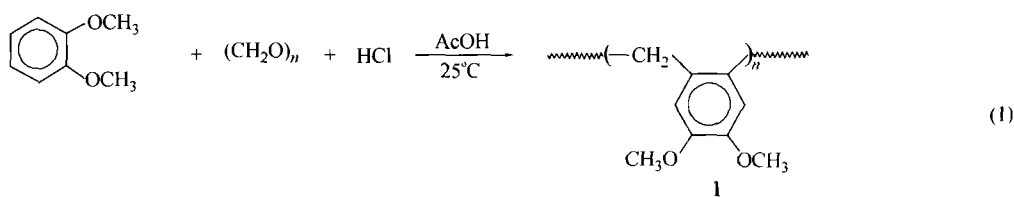
An amount of 0.02 g of poly(3,4-dihydroxy-*o*-tolylene) was dissolved in 150 mL of glacial acetic acid (90%) in a thermostated electrolytic cell fitted with a magnetic stirrer and the two above-mentioned electrodes. Prior to the titration, the solution was bubbled with a stream of nitrogen for 30 min to flush the dissolved oxygen. The potentiometric titration was performed with 0.05 N ceric ammonium nitrate in acetic acid (90%) at 25°C and under nitrogen stream. Readings of the potential were recorded in millivolts.

RESULTS AND DISCUSSION

Synthesis of Poly(3,4-dimethoxy-*o*-tolylene)

The high vulnerability of the benzene compounds bearing electron-donating groups toward Friedel-Crafts reaction is considered to be advantageous for preparing condensation redox polymers. Soluble redox polymers have been usually desired to estimate their redox properties in solution media^[1]. In fact, reliable potentiometric titration results of insoluble counterparts were burdened by their insolubility and, frequently, a soluble mediator was always required^[8,9]. However, soluble poly(3,4-dihydroxy-*o*-tolylene) could not be directly obtained from its bare monomer, catechol, under the conditions shown in Eq. (1), but rather resole-type resins are obtained.

An efficient alternative is to use their dimethoxy precursors in the reaction, and thus, to reduce the great electron-releasing capacity of the bare dihydroxy group. Indeed, when 1,2-dimethoxybenzene (veratrole) was subjected to chloromethylation reaction as shown in Eq. (1), a chloroform-soluble white precipitate **1** was formed. The formation of this product seemed to be temperature dependent; only at temperatures above 5°C can this product be formed and precipitated.



Along with the white precipitate **1**, a semi-solid tacky material was isolated from the liquid medium by extraction with diethyl ether. The mechanism for the formation of the white precipitate and this semi-solid substance is believed to occur through the Friedel-Crafts reaction sequences hinting at the reactivity of the dimethoxybenzene.

The formed white precipitate **1** shows a peculiar solubility; it is soluble only in chloroform among other organic solvents. Poly(2,5-dimethoxy-*p*-xylylene) was reported earlier to be soluble exclusively in bromoform^[10]. The intrinsic viscosities of the white polymer **1** and the semi-solid material were rather low, 0.034 and 0.013 dL · g⁻¹, respectively. Linear soluble polybenzyls formed upon reacting 1,2,4,5-tetrasubstituted benzene with formaldehyde in chloroform in the presence of trifluoroacetic acid were reported to have low molecular weights^[11]. It is interesting to recall that the poly(*p*-xylylene)s, (PPXs), prepared by other methods always have low molecular weights^[12-16].

The infrared spectra of white polymer and the semi-solid resin are shown in Fig. 1. The IR spectrum of the resin differs from those of veratrole and the white polymer. Indeed, two additional bands at 1750 and 850 cm⁻¹ are detected in the IR spectrum of the resinous material. The band at 1750 cm⁻¹ can be assigned to the carbonyl of the possibly formed acetylated group, such as —CH₂OOCCH₃, this group could probably stem from an esterification reaction between the *in situ*-formed methylol moiety and the acetic acid used as a medium for the reaction. Thus, the chemical structure of the semi-solid is somewhat different from that of the white polymer.

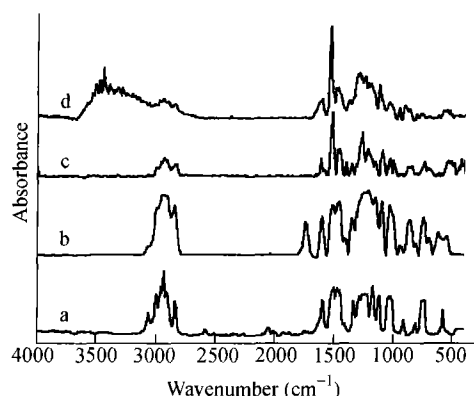


Fig. 1 Infrared spectra of (a) prepared 1,2-dimethoxybenzene, (b) semi-solid resin, (c) poly(3,4-dimethoxy-*o*-tolylene) and (d) poly(3,4-dihydroxy-*o*-tolylene)

The DSC thermogram of the white polymer is given in Fig. 2 and the results are compiled in Table 1. As it can be seen, the glass transition temperature of **1** was about 232°C. Poly(2,5-dimethoxy-*p*-xylylene) was reported to soften at 235°C^[10]. This high T_g , compared to those of poly(dialkoxystyrene)s ($T_g \cong 100\text{--}125^\circ\text{C}$)^[17], could be due to the benzene rings present within the polymer backbone. The benzene rings stiffen the polymer matrix and therefore make the polymer chains to move difficultly. The sharp exothermic peak at 340°C, was taken as the crystallization temperature T_c , which could be related to the crystallization of the polymer during the thermal process, and a certain extent of crystallinity was hence ensued. The resulted crystalline portion of the polymer melted at $T_m = 412^\circ\text{C}$ as shown by an endothermic peak. The ratio T_c/T_g is found to be 1.215 and this is in good agreement with the reported relationship $T_c = 1.125 T_g$ ^[17]. The ratio T_g/T_m is 0.74 which is very close to the value expected for condensation polymers as the Beaman-Boyer empirical rule suggested^[18].

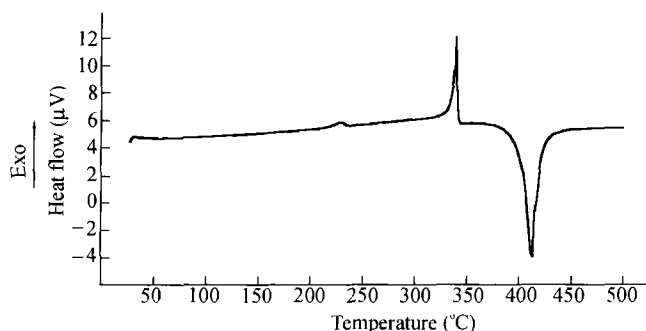


Fig. 2 Differential scanning calorimetry thermogram of poly(3,4-dimethoxy-*o*-tolylene) **1**

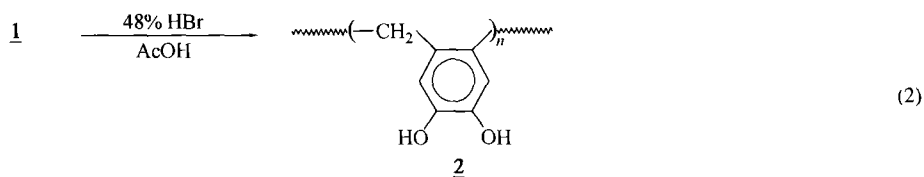
Table 1. Results of the synthesis and characterization of poly(3,4-dimethoxy-*o*-tolylene)

Yield (%)	$[\eta]$ (dL g ⁻¹)	M_v	T_g (°C)	T_c (°C)	T_m (°C)
20.60	0.034	3125	232	340	412
	(0.013)*	950	—	—	—

*The intrinsic viscosity of the semi-solid resin

Poly(3,4-dihydroxy-*o*-tolylene)

The removal of methoxy groups in **1** was effected by 48% HBr and resulted in the formation of poly(3,4-dihydroxy-*o*-tolylene) **2** as traced in Eq. (2). The demethylated polymer **2** was insoluble in common organic solvents but soluble in methanol. Like poly(2,5-dihydroxy-*p*-xylylene)^[10], the cleaved **2** was green. From Fig. 1 the spectra patterns are quite different; absorption band of O—H of the dihydroxylated products clearly appeared at 3200–3500 cm⁻¹.



A feature of poly(dihydroxy-*o*-tolylene) 2 was its pronounced air-oxidation resistance within a long period of time. The poly(vinylcatechol) and poly(vinylhydroquinone) were reported to be prone to such oxidation phenomenon yielding colored and insoluble materials^[11, 19].

Potentiometric titration of Poly(3,4-dihydroxy-*o*-tolylene) 2

Catechol and the poly(3,4-dihydroxy-*o*-tolylene) 2 were potentiometrically titrated at 25°C with 0.05 N ceric ammonium nitrate in 90% acetic acid under nitrogen atmosphere. The redox process implying an electron transfer is illustrated in Eq. (3). The potentiometric titrations of catechol/poly(3,4-dihydroxy-*o*-tolylene) are plotted in Fig. 3.

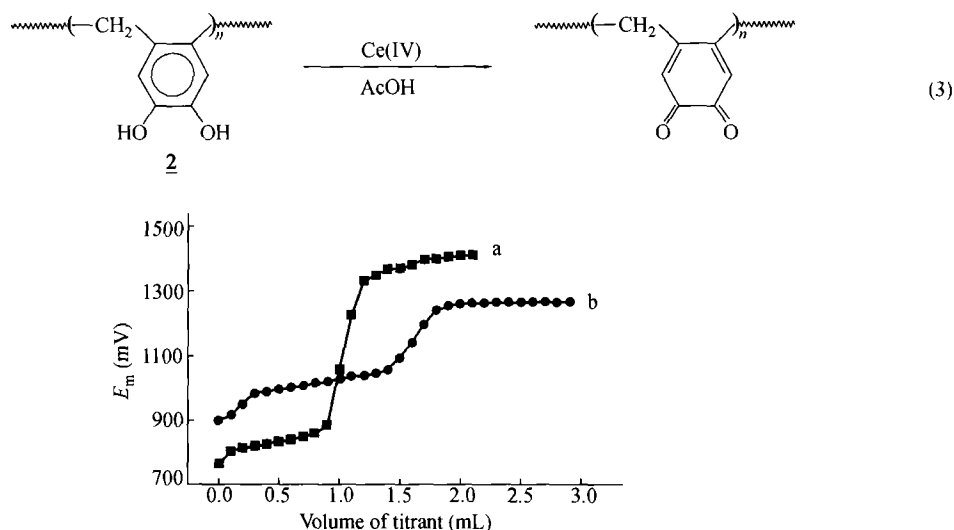


Fig. 3 Plots of the potentiometric titration at 25°C with 0.05 N ceric ammonium nitrate in 90% acetic acid
a) Catechol; b) Poly(3,4-dihydroxy-*o*-tolylene) 2

The “polymeric effect” is manifested on two aspects of the titration of poly(3,4-dihydroxy-*o*-tolylene). The first one was that the potentials during the titration of polymers took a long duration to stabilize. As observed earlier^[19, 20] the potentials during the titration of catechol and hydroquinone were read within 3–5 min. However, a delay in the establishment of stable potentials was noted for their corresponding polymers; it might take 30–40 min to attain stable potentials. Cassidy ascribed this slowness to the redistribution of the oxidized sites; that is, upon addition of the titrant, the redox reaction was expectedly rapid, but the equilibrium could be reached only at longer times because of the propagation process throughout the polymeric chain^[21].

The second aspect was the higher midpotential E_m of the polymer compared to that of catechol. From Fig. 3 the E_m s of the catechol and its corresponding polymer can be deduced to be 832 and 1017 mV, respectively. As can be seen, the midpotential of the polymer was 185 mV higher than that of the monomeric one, catechol. Even though a higher midpotential of the polymer compared to that of its monomeric analogue was a common observation to Cassidy and Iwabushi^[9, 21], the reported difference however was only 30 mV. This relatively high potential of the redox polymer is believed to be associated with a “polymeric effect” factor, the oxidized form of the redox resin tended to adhere to the indicator electrode (platinum electrode), therefore, the potential would rise.

CONCLUSION

Soluble poly(3,4-dihydroxy-*o*-tolylene) and its precursor were prepared with no major difficulty. Yet, the molecular weight of the polymer precursor was very low and, therefore, a method for making this precursor in a higher molecular weight form is sought for. The redox midpotential of the poly(3,4-dihydroxy-*o*-tolylene) was found unexpectedly higher than that of the monomer, catechol, implying a greater redox activity of the polymer.

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