

# Synthesis of New Electron Transfer Polymers for the Reduction of Dissolved Oxygen in Water

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**ABSTRACT:** Polymers based upon hydroquinone–quinone redox system were prepared by the addition of hydroquinone and methylhydroquinone to parachloromethylstyrene. Others were obtained by vinylation of halogenated compounds and polymerization of monomers containing the redox system. In the last case, composition and structure of macromolecules are known with increased certainty and so, they are readily characterized. For the first time, preparation and polymerization of monomers are realized with good yields. By using these macromolecules to remove oxygen from water, it was established that redoxite properties of Electron Transfer Polymers (ETP) have been closely related to the number of redox functions on the polymer matrix. © 2001 John Wiley & Sons, Inc. *J Appl Polym Sci* 80: 223–229, 2001

**Key words:** electron transfer polymers; dissolved oxygen; macromolecule structures

## INTRODUCTION

One of our research projects concerns the syntheses of new macromolecules (containing ionic metal transition, redox polymers, etc.) by polymerization of functionalized monomers.<sup>1</sup> Investigations into reduction of dissolved oxygen by Electron Transfer polymers (ETP) have received considerable attentions.<sup>2–12</sup> Most of the substances based upon hydroquinone–quinone redox system were prepared by Friedel-Crafts alkylation of hydroquinone, benzoquinone, *p*-dimethoxybenzene, *p*-diacetoxybenzene to styrene divinylbenzene copolymers<sup>13</sup> or to chloromethylated polystyrene resins.<sup>14</sup> Then, they were functionalized by the addition of electron donors and/or hydrophilic groups<sup>15</sup> to increase their redox properties. This procedure is a convenient method to obtain the new material with only 60 to 80% of

grafted redox functions but not to produce highly grafted redox polymers.

One area of interest is the reduction of oxygen in organic liquids and water. The corrosive effect of dissolved oxygen in boiler water requires, in fact, the removal of oxygen to near-zero levels. Because the last studies have clearly demonstrated the reduction of oxygen, dissolved in water and organic liquids, by redox polymers, we thought that it could be interesting to produce highly grafted ETP and to compare the efficiency of these polymers with the known results.

In this article, we report the preliminary studies on syntheses, characterizations of monomers and polymers, and results of oxygen removal from water.

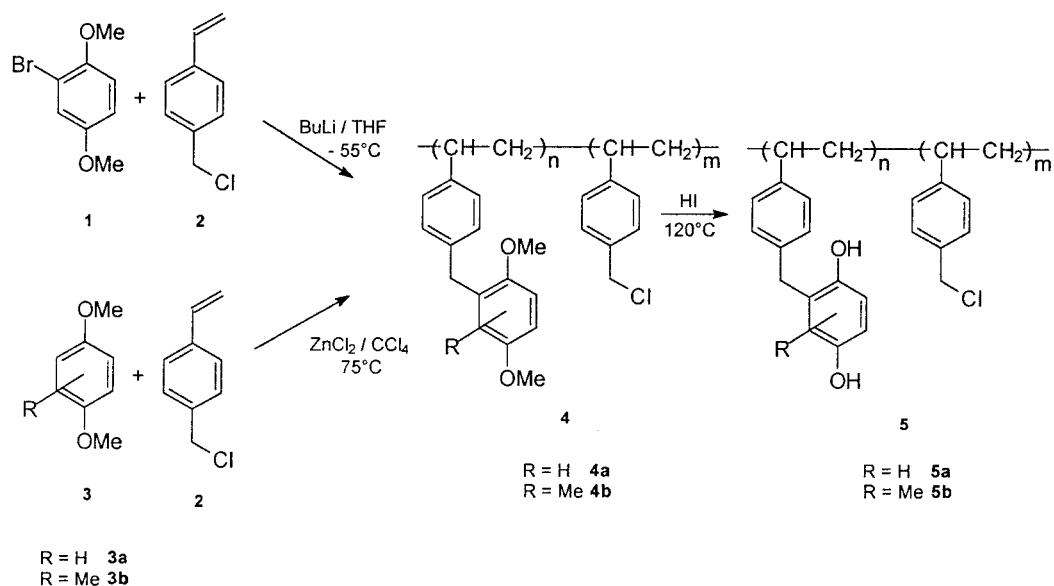
There are two approaches that can be applied to produce the ETP: (1) to synthesize polymers by alkylation reaction, (2) to synthesize specific monomers containing *p*-dimethoxybenzene and then polymerize them.

The first approach, as illustrated in Scheme 1, is to prepare a highly grafted Electron Transfer

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Scheme 1

Polymer in 2 steps with molar ratios:  $1/2 = 1/1$  and  $3/2 = 1/1$ . The second approach (Scheme 2) needs a polymerization method of specific monomers to synthesize functionalized polystyrene with a maximal density of redox functionalities.

## RESULTS AND DISCUSSION

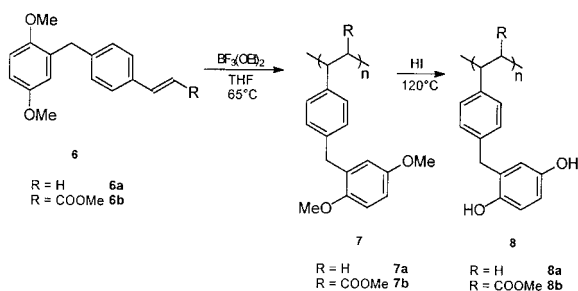
### Synthesis and Characterization of Polystyrenes

The basic strategies employed for synthesizing polymers are based upon alkylation and lithiation reactions. After the reaction, the organic mixture was poured onto a mixture of ice and hydrochloric acid. The polymers **4a** and **4b** (Scheme 1) were obtained in a satisfactory yield (about 80%). Cleavage of methoxy groups was achieved by addition of 47% hydriodic acid on the macromole-

cules. Electron Transfer Polymers **5a** and **5b** (Scheme 1) were isolated with about 70% yield.

By using butyllithium as reactant, polymers **4a** and poly-(*p*-chloromethyl)styrene were obtained (Fig. 1). The poly-(*p*-chloromethyl)styrene was characterized by the chemical shifts (46–48 ppm) of the chloromethylene groups. Poly-(*p*-chloromethyl)styrene was not identified by  $^{13}\text{C}$ -NMR (Fig. 2) when the polymer **4a** was synthesized by the Friedel-Crafts reaction.

Polymer **4b** was obtained by the Friedel-Crafts reaction (Scheme 1).  $^{13}\text{C}$ -NMR spectrum shows the lack of poly-(4-chloromethyl)styrene (Fig. 3). Thus, the nature of polymers appeared to be controlled mainly by the two factors: the catalyst,



Scheme 2

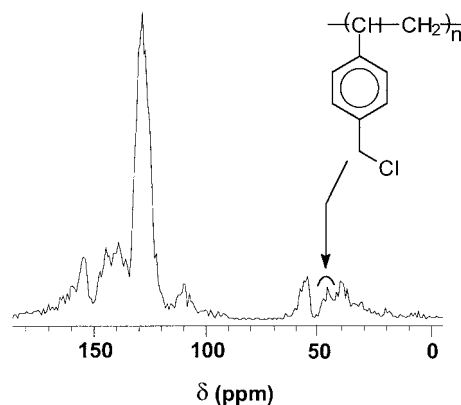
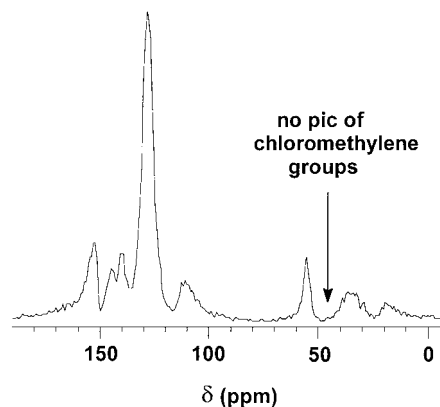


Figure 1  $^{13}\text{C}$ -NMR spectrum of a mixture of **4a** and poly-(*p*-chloromethyl)styrene).



**Figure 2**  $^{13}\text{C}$ -NMR spectrum of polymer **4a**.

and the reaction temperature (Table I). On the other hand, the substitution of 2,5-dimethoxy-toluene **3b** occurred at the *para* and *meta* positions of methyl group (Scheme 3). Polymer **4b** appears as a mixture of two polymers, **4b'** and **4b''** (Scheme 3). Structure of these polymers are confirmed by  $^{13}\text{C}$ -NMR shifts at 54.5 and 60.1 ppm, respectively, of methoxy groups (Fig. 4). For our application, it was not necessary to isolate each of these polymers.

Polymers **7a** and **7b** were synthesized by polymerization of specific monomers **6a** and **6b** (Scheme 2). These monomers were obtained by vinylation of 2,5-dimethoxy-1-(4'-iodobenzyl)benzene (Scheme 4). The methoxy groups of these polymers were removed by addition of 47% hydriodic acid<sup>3</sup> or bromhydric acid<sup>4</sup> to give the Electron Transfer Polymers **8a** and **8b** (Scheme 2) with a maximal density of hydroquinone on the polystyrene matrix.

### Redox Properties of the Resins

Four different physical structures of Electron Transfer Polymer were used to reduce dissolved oxygen in water. Redox polymers varied in concentration of reacted hydroquinone (Table II). To remove oxygen from water, air was first of all bubbled through a NaOH solution (pH = 9) to give  $[\text{O}_2] = 9$  ppm and a hydroquinone to oxygen molar ratio 2.5 : 1 was used. Figure 5 shows the rate of oxygen removal from water under basic solution. For the first time, results seem to indicate the oxygen content of water may be reduced to less than 0.5 ppm in approximately 2.5 min. The rate of oxygen consumption increases with an increase in the number of hydroquinone on the polymer matrix. Though the methylated hydroqui-

none resin **5b** showed redox properties, the rate of attainment of the maximum redox capacities were better than the unsubstituted hydroquinone resins **5a**, **8a**, and **8b**. Thus, an increase in quinone stability is reflected by an increase in the reactivity of the corresponding hydroquinone.<sup>9</sup>

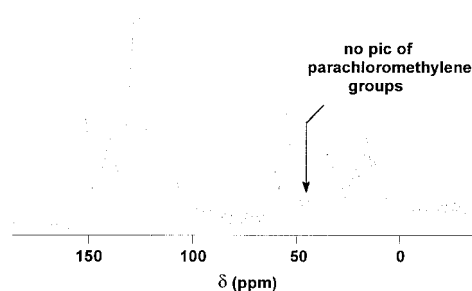
## CONCLUSION

New redox polymers were prepared by vinylation of 2,5-dimethoxy-1-(4'-iodobenzyl)benzene, polymerization, and demethylation of the methoxy groups with good yields. Others were produced by alkylation of *p*-chloromethylstyrene and *p*-dimethoxybenzene. It was established that redox properties of the different polymers were closely linked to the number of redox functions on the polymer matrix.

## EXPERIMENTAL

### Materials

$^1\text{H}$ -NMR 300.133 MHz spectra were run on a Brücker AC300 spectrometer with TMS as an internal reference. The products were dissolved in the mentioned solvent. Data are given in the following order: chemical shift in ppm, multiplicity (s, singlet; d, doublet; dd, double-doublet), coupling constant in Hertz, assignment.  $^{13}\text{C}$ -NMR spectra were determined at 75.47 MHz with a Brücker AC300 spectrometer with TMS as an internal reference. The solvent used is indicated below. For polymers,  $^{13}\text{C}$ -NMR spectra were run on a Brücker ASX100 spectrometer at 25,18 MHz without solvent. IR absorption spectra were recorded as solids in KBr pellets on a Brücker IFS48 Fourier transform spectrophotometer. The mentioned IR absorption were observed as strong



**Figure 3**  $^{13}\text{C}$ -NMR spectrum of polymer **4b**.

Table I

Polymers	Catalyst	Solvent	Elemental Analysis				Grafting Rate
			C%	H%	Cl%	O%	
<b>4a</b>	BuLi	THF	70.95	6.90	6.79	12.70	38.7
<b>4a</b>	ZnCl <sub>2</sub>	CH <sub>2</sub> Cl <sub>2</sub>	77.55	6.86	5.54	10.15	50
<b>4a</b>	ZnCl <sub>2</sub>	CCl <sub>4</sub>	80.80	6.90	0.33	11.97	97.67
<b>4b</b>	ZnCl <sub>2</sub>	CCl <sub>4</sub>	70.49	7.43	0.49	11.49	96.3

bands in cm<sup>-1</sup>. Elemental analyses were performed by "Service Central de Microanalyses" of CNRS, in Vernaison, France. These results allowed to determine the values for "n" and "m" for the reaction products. Melting points were determined with a Metler FP1 and are uncorrected.

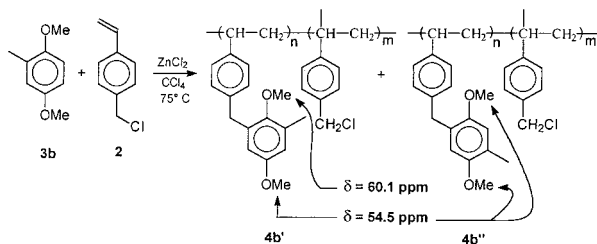
### Synthesis of 1-Bromo-2,5-dimethoxybenzene 1

1,4-Dimethoxybenzene (5 g, 36.2 mmol) in acetonitrile (150 mL) was stirred at room temperature until complete dissolution. NBS (5.2 g, 36.2 mmol) was added and the reaction mixture was stirred at room temperature for 6 h. The mixture was concentrated under vacuum. The residue was washed with water (50 mL) and extracted with diethyl ether 30 mL). The organic layer was dried and concentrated under vacuum. The residue was purified by distillation. Yield 80%, *E* = 130°C/130 mmHg.

<sup>1</sup>H-NMR (CDCl<sub>3</sub>): 3.72 (s, 3H), 3.83 (s, 3H), 6.78 (m, 2H), 7.10 (dd, *J* = 2.4 Hz, *J* = 0.9 Hz, 1H); <sup>13</sup>H-NMR (CDCl<sub>3</sub>): 55.8, 56.8, 111.9, 112.9, 113.6, 119.0, 150.2, 154.0.

### Synthesis of 2,5-Dimethoxy-1-(4'-iodobenzyl)benzene 9

Triflic acid (1.32 g, 9.0 mmol) was added (syringe) at room temperature, to a stirred solution of 2,5-dimethoxy-4'-iodobenzhydrol<sup>16</sup> (10 g, 27.1 mmol)



Scheme 3

in dichloromethane (80 mL). A solution of triethylsilane (7.86 g, 67.5 mmol) in dry dichloromethane (20 mL) was added dropwise. An exothermic reaction takes place while the temperature is maintained at 20°C. After 45 min, the mixture was poured into cold saturated sodium hydrogen carbonate solution (100 mL) and extracted with dichloromethane (3 × 30 mL). The organic layer was dried with magnesium sulfate, and concentrated under vacuum. Solid product can be purified by crystallization in petroleum ether and diethyl ether mixture. Yield = 90%, white powder, *F* = 60°C.

<sup>1</sup>H-NMR (CDCl<sub>3</sub>): 3.74 (s, 3H), 3.76 (s, 3H), 3.89 (s, 2H), 6.66 (d, *J* = 2.8 Hz, 1H), 6.74 (dd, *J* = 8.8 Hz, *J* = 2.8 Hz, 1H), 6.80 (d, *J* = 8.8 Hz, 1H), 6.98 (d, *J* = 8.2 Hz, 2H), 7.60 (d, *J* = 8.2 Hz, 2H); <sup>13</sup>H-NMR (CDCl<sub>3</sub>): 35.7, 55.7, 56.0, 91.4, 111.4, 116.9, 130.5, 131.0, 137.3, 140.9, 152.1, 153.8; IR (KBr pellets): 523, 1049, 1224, 1430, 1450, 1501, 1587, 2827, 2935, 2995; Elemental analysis of C<sub>15</sub>H<sub>15</sub>IO<sub>2</sub>, Calcd: C, 50.87%; H, 4.27%; O, 9.03%. Found: C, 50.82%; H, 4.35%; O, 8.95%.

### Synthesis of Monomers 6a and 6b

#### Preparation of 2,5-Dimethoxy-1-(4'-vinylbenzyl)benzene 6a

Trimethylvinylsilane (3.39 g, 33.8 mmol) was slowly added to a solution of 2,5-dimethoxy-1-(4'-

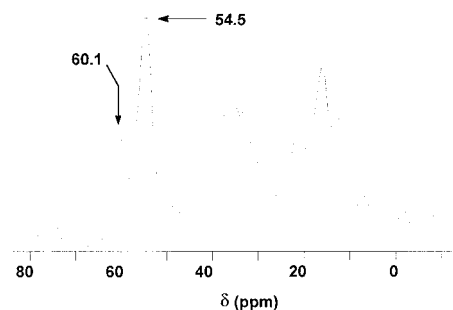
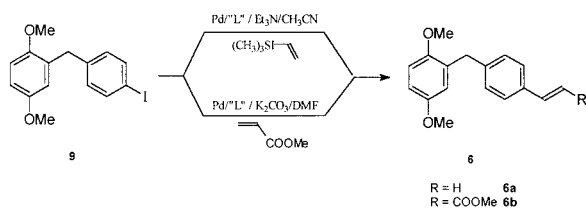


Figure 4 <sup>13</sup>C-NMR spectrum of polymer **4b** between 0–80 ppm.



Scheme 4

iodobenzyl)benzene (6 g, 16.9 mmol), triphenylphosphine (0.53 g, 2 mmol) with palladium acetate (0.22 g, 1 mmol) in triethylamine (3 mL) and acetonitrile (70 mL). The reaction mixture was heated at 90°C for 12 h and the catalyst was collected. After washing the solution with water (30 mL), the organic layer was extracted with diethyl ether (3 × 20 mL), dried with sodium sulfate, and concentrated giving a brown oil. Yield = 86%.

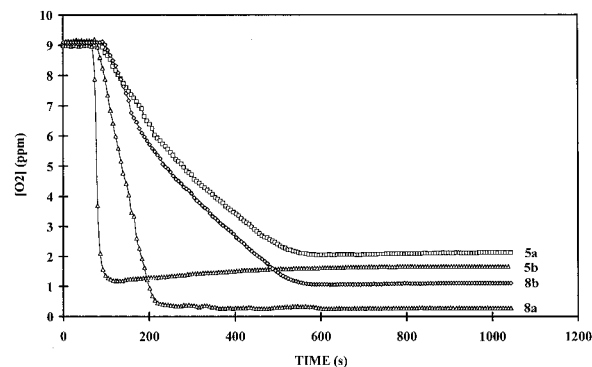
<sup>1</sup>H-NMR (CDCl<sub>3</sub>): 3.74 (s, 3H), 3.78 (s, 3H), 3.98 (s, 2H), 5.21 (d, *J* = 10.9 Hz, 1H), 5.73 (d, *J* = 17.6 Hz, 1H), 6.64 (dd, *J* = 17.6 Hz, *J* = 10.9 Hz, 1H), 6.66 (d, *J* = 2.8 Hz, 1H), 6.74 (dd, *J* = 8.8 Hz, *J* = 2.8 Hz, 1H), 6.82 (d, *J* = 8.8 Hz, 1H), 7.22 (d, *J* = 8.0 Hz, 2H), 7.36 (d, *J* = 8.0 Hz, 2H); <sup>13</sup>H-NMR (CDCl<sub>3</sub>): 35.8, 55.6, 56.0, 91.4, 111.2, 111.4, 113.0, 116.8, 126.2, 129.1, 130.8, 136.7, 143.5, 151.7, 153.5.

#### Preparation of Methyl 4-(2,5-dimethoxybenzyl)cinnamate 6b

A mixture of 2,5-dimethoxy-1-(4'-iodobenzyl)benzene **9** (15 g, 42.4 mmol), of methyl acrylate (7.3 g, 84.8 mmol), of carbonate de potassium (15.8 g, 114.3 mmol), of catalyst K<sub>10</sub>-Pd-Cu<sup>17</sup> (1.5 g), and 100 mL of dimethylformamide was refluxed for 2 h. The catalyst was collected, and the cooled reaction mixture was stirred with 100 mL of water. The organic layer was extracted with dichloromethane (50 mL) and dried over CaCl<sub>2</sub>. The organic solvents were removed and the product was purified by reprecipitation from heptane to

Table II

Polymers	R	% Hydroquinone
<b>5a</b>	H	97.7
<b>5b</b>	Me	96.3
<b>8a</b>	H	100
<b>8b</b>	COOMe	100



**Figure 5** Oxygen removal from water by using different hydroquinone redox polymers.

give the monomer. Yield = 93%, white powder, *F* = 83°C.

<sup>1</sup>H-NMR (CDCl<sub>3</sub>): 3.72 (s, 3H), 3.76 (s, 3H), 3.79 (s, 3H), 3.95 (s, 2H), 6.38 (d, *J* = 16.1 Hz, 1H), 6.66 (d, *J* = 3.0 Hz, 1H), 6.72 (dd, *J* = 8.8 Hz, *J* = 3.0 Hz, 1H), 6.79 (d, *J* = 8.8 Hz, 1H), 7.22 (d, *J* = 8.1 Hz, 2H), 7.42 (d, *J* = 8.1 Hz, 2H), 7.66 (d, *J* = 16.1 Hz, 1H); <sup>13</sup>H-NMR (CDCl<sub>3</sub>): 36.1, 51.7, 55.7, 56.0, 111.5, 116.9, 128.2, 128.4, 130.2, 132.1, 143.7, 144.9, 151.7, 153.6, 167.7; IR (KBr pellets): 1020, 1168, 1228, 1321, 1429, 1500, 1600, 1710, 2835, 2994; Elemental analysis of C<sub>19</sub>H<sub>20</sub>O<sub>4</sub>, Calcd: C, 73.06%; H, 6.45%. Found: C, 72.92%; H, 6.29%.

#### Preparation of Poly-methyl-4-(2,5-dimethoxybenzyl)cinnamate 7b

A solution of BF<sub>3</sub>(OEt)<sub>2</sub> (14.6 g, 103 mmol) was added to a solution of methyl-4-(2,5-dimethoxybenzyl)cinnamate (8 g, 25.6 mmol) in tetrahydrofuran (50 mL) at room temperature. The mixture was stirred at 65°C for 48 h, and was concentrated under vacuum. After washing the residue with a solution of 1 M Na<sub>2</sub>CO<sub>3</sub>, the organic layer was extracted with dichloromethane (50 mL), dried over CaCl<sub>2</sub> and concentrated under vacuum to give **7b** (6.5 g, 80%) as a brown solid, m.p. 79–80°C; IR (KBr): 2990, 2940, 2838, 1598, 1510, 1450, 1220 cm<sup>-1</sup>.

#### Synthesis of Redox Polymers by Friedel-Crafts Reaction

##### Preparation of Poly-4-(2,5-dimethoxybenzyl)styrene 4a

To a stirred solution of anhydrous ZnCl<sub>2</sub> (9.90 g, 72.6 mmol) in dry carbon tetrachloride (50 mL),

under an inert atmosphere of nitrogen, paradimethoxybenzene (10 g, 72.5 mmol) was added portion-wise. The mixture was then heated to 75°C before adding 4-chloromethylstyrene (11.1 g, 72.5 mmol) and was stirred for overnight. It was then poured into a mixture of HCl 1 M (100 mL) and crushed ice to decompose the zinc complex. Rapid crystallization of polymer occurred. The precipitate was collected then washed with H<sub>2</sub>O (3 × 40 mL). After drying under vacuum, the polymer **4a** was isolated, yield = 76%, pink powder, *n* = 42, *m* = 1 (Table I).

<sup>13</sup>C-NMR: 21.0, 37.4, 55.2, 111.4, 128.6, 138.4, 140.0, 151.4; IR (KBr pellets): 1046, 1211, 1400, 1457, 1505, 1606, 2827-2950.

#### Preparation of Poly-4-(2,5-dimethoxytoluyl)styrene **4b**

To a stirred solution of anhydrous ZnCl<sub>2</sub> (9.90 g, 72.6 mmol) in dry carbon tetrachloride (50 mL), under an inert atmosphere of nitrogen, 2,5-dimethoxytoluene (11 g, 72.5 mmol) was added portion-wise. The mixture was then heated to 75°C before adding 4-chloromethylstyrene (11.1 g, 72.5 mmol) and was stirred for overnight. It was then poured into a mixture of HCl 1 M (100 mL) and crushed ice to decompose the zinc complex. Rapid crystallization of polymer occurred. The crude product was recovered by filtration on a glass filter, washed with ethanol (2 × 40 mL) and dried *in vacuo*. Yield = 70%, yellow powder, *n* = 26, *m* = 1 (Table I).

<sup>13</sup>C-NMR: 16.1, 22.0, 36.8, 54.7, 60.1, 112.5, 128.0, 140.0, 141.5, 151.5; IR (KBr pellets): 1046, 1209, 1399, 1463, 1506, 1602, 2827-2932.

Polymer **4b** appears as a mixture of two polymers **4b'** (45%) and **4b''** (55%) (Scheme 2).

#### Synthesis of Poly-4-(2,5-dimethoxybenzyl)styrene **4a** Using Butyllithium as Catalyst

To a stirred solution of 1-bromo-2,5-dimethoxybenzene **1** (7.2 g, 32.8 mmol) in dry THF (50 mL), under an inert atmosphere of nitrogen, butyllithium was added (syringe) at -55°C. After complete disparition of **1**, *p*-chloromethylstyrene (5 g, 32.8 mmol) was added dropwise at room temperature and the mixture was heated to 70°C for 24 h. The mixture was poured into a mixture of HCl 1 M (100 mL), and the organic layer was extracted with dichloromethane (50 mL). The mixture was concentrated under vacuum, and methanol was added to the residue. After filtra-

tion, the polymer **4a** was isolated, yield = 50%, pink powder (Table I).

#### Acid Cleavage of the *p*-Dimethoxybenzene Adduct to Give Polyvinylbenzylhydroquinone

##### General Procedure

To the beads from the above reactions was added a solution of 47% hydriodic acid. The mixture was stirred and heated at reflux temperature, 110°C for 16 h. The organic layer was washed with deionized water until the washing were neutral to pH paper, and then dried to constant weight.

##### Polyvinylbenzylhydroquinone **5a**

Yield = 92%, white powder, *n* = 42, *m* = 1.

IR (KBr pellets): 3529 (O—H), 2926, 1652, 1605, 1507, 1450, 1209.

##### Polyvinylbenzyltoluhydroquinone **5b**

Yield = 77%, white powder, *n* = 26, *m* = 1.

IR (KBr pellets): 3529 (O—H), 2963, 2929, 1601, 1508, 1460, 1194.

##### Polyvinylbenzylhydroquinone **8a**

Yield = 92%, brown powder.

IR (KBr pellets): 3424 (O—H), 2931, 1654, 1601, 1510, 1452, 1207. Elemental analysis of **8a**, Calcd: C, 79.62%; H, 6.23%. Found: C, 79.41%; H, 6.29%.

##### Poly-methyl-4-(2,5-dihydroxybenzyl)cinnamate **8b**

Yield = 73%, brown powder.

IR (KBr pellets): 3224 (O—H), 2981, 2941, 1735, 1633, 1605, 1505, 1210. Elemental analysis of **8b**, Calcd: C, 71.82%; H, 5.67%. Found: C, 71.34%; H, 6.18%.

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