

## **Phase transfer catalyzed polymerization of 4-hydroxy-3,5-dimethylbenzyl alcohol and copolymerization of 4-bromo-2,6-dimethylphenol with 4-hydroxy-3,5-dimethylbenzyl alcohol**

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### SUMMARY

This paper describes the phase transfer catalyzed (PTC) polymerization of 4-hydroxy-3,5-dimethylbenzyl alcohol (**1**) and the PTC polymerization of 4-bromo-2,6-dimethylphenol (**19**) in the presence of 4-hydroxy-3,5-dimethylbenzyl alcohol (**1**). At 89% conversion the homopolymerization of **1** produced a 95% yield of 4,4'-dihydroxy-3,3',5,5'-tetramethyldiphenylmethane (**3**) and a 5% yield of oligomers. The polymerization of **19** in the presence of **1** resulted in poly(2,6-dimethyl-1,4-phenylene oxide) (PPO) polymers in 71 to 89% yields. The 200 MHz <sup>1</sup>H-NMR spectroscopy analyses of the resulting PPO polymers indicate that they represent a mixture of bifunctional (PPO-2OH) and monofunctional (PPO-OH) polymers. A radical-anion mechanism was proposed to account for both the homopolymerization and the copolymerization reactions.

### INTRODUCTION

So far two mechanisms have been proposed for the synthesis of poly(2,6-dimethyl-1,4-phenylene oxide) (PPO). A radical-radical mechanism is responsible for the polymerization of 2,6-dimethylphenol in the presence of a copper-amine complex catalyst.<sup>1-8</sup> The radical-anion mechanism accounts for the polymerization of 4-bromo-2,6-dimethylphenol under both phase transfer catalyzed (PTC) and non-phase transfer catalyzed two-phase reaction conditions.<sup>1-5,7,9</sup> A novel radical-anion PTC polymerization of 4-bromo-2,6-dimethylphenol in the presence of either 2,4,6-trimethylphenol or 4-tert-butyl-2,6-dimethylphenol has been recently developed.<sup>10</sup> PPO polymers with one phenol chain end (PPO-OH) and controlled molecular weights can be obtained by this method.

A radical-anion mechanism was also suggested to be responsible for the PTC depolymerization of high molecular weight PPO-OH polymers in the presence of either 2,4,6-trimethylphenol or 4-tert-butyl-2,6-dimethylphenol.<sup>11,12</sup> The radical-anion mechanism has recently been applied to the synthesis of PPO polymers with two phenol chain ends (PPO-2OH), which consists of the PTC polymerization of 4-bromo-2,6-dimethylphenol in the presence of 2,2-di(4-hydroxy-3,5-dimethylphenyl)propane.<sup>13</sup>

2,4,6-Trimethylphenol was reported to undergo oxidative dealkylation when treated with excess manganese dioxide.<sup>14</sup> This reaction produced a mixture of PPO-OH and 4,4'-dihydroxy-3,3',5,5'-tetramethyldiphenylmethane. The proposed mechanism assumed a two-electron oxidation leading to a quinone methide intermediate, which subsequently generates 4-hydroxy-3,5-dimethylbenzyl alcohol. However, previous results from our laboratory<sup>10</sup> have demonstrated that under PTC reaction conditions 2,4,6-trimethylphenol remains mostly unreacted (97%). Under these conditions 2,4,6-trimethylphenol led to 3% oligomers only.

The first goal of this paper is to describe the phase transfer catalyzed homopolymerization of the proposed intermediate, 4-hydroxy-3,5-dimethylbenzyl alcohol, generated during the severe oxidative reactions of 2,4,6-trimethylphenol. The second goal of this paper is to discuss the polymerization of 4-bromo-2,6-dimethylphenol in the presence of 4-hydroxy-3,5-dimethylbenzyl alcohol under phase transfer catalyzed reaction conditions.

### EXPERIMENTAL

#### Materials

4-Bromo-2,6-dimethylphenol (97%, Aldrich) was recrystallized from petroleum ether. 2,6-Dimethylphenol (99.8+%, Aldrich), tetrabutylammonium hydrogen sulfate (TBAH) (97%, Aldrich), and all the other reagents were used as received.

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### Techniques

200 MHz  $^1\text{H-NMR}$  spectra (TMS,  $\delta$ , ppm) were recorded on a Varian XL-200 spectrometer. All spectra were recorded in  $\text{CDCl}_3$  with TMS as the internal standard. Gel Permeation Chromatography (GPC) measurements were performed on a Perkin-Elmer series 10 LC instrument equipped with an LC-100 column oven, an LC 600 autosampler, and a Nelson Analytical 900 series data station. The measurements were made using a UV detector set at 254 nm, chloroform as solvent (1 mL/min,  $40^\circ\text{C}$ ), a set of PL-gel columns (500 and  $10^4$  Å), and a calibration plot constructed with polystyrene standards (Supelco). Purity was similarly determined by high pressure liquid chromatography (HPLC)/GPC using a 100 Å PL-gel column.

#### Synthesis of 4-Hydroxy-3,5-dimethylbenzaldehyde

4-Hydroxy-3,5-dimethylbenzaldehyde was synthesized according to a literature procedure.<sup>15</sup> Purity (HPLC): >99.9%.  $^1\text{H-NMR}$ : 2.31 (s, Ph- $\text{CH}_3$ , 6H), 5.23 (s, Ph-OH), 7.54 (s, 2 aromatic protons), 9.81 (s, Ph-CHO).

#### Synthesis of 4-Hydroxy-3,5-dimethylbenzyl Alcohol

4-Hydroxy-3,5-dimethylbenzaldehyde (4.47 g, 29.8 mmol) was dissolved in 100 mL methanol, cooled to  $-10^\circ\text{C}$ , and a solution of sodium borohydride (1.47 g, 38.7 mmol) in 9 mL 0.45 N aqueous NaOH was added dropwise. The reaction mixture was then stirred at room temperature for 1 h. After removing methanol on a rotovapor, the residue was poured into 300 mL cold water and extracted 5 times with chloroform. The condensed residue was recrystallized from hexane to yield 3.12 g (75%) of **3**; purity: 99.0%.  $^1\text{H-NMR}$ : 2.25 (s, Ph- $\text{CH}_3$ , 6H), 4.51 (s, Ph- $\text{CH}_2\text{OH}$ ), 4.62 (s, OH), 6.98 (s, 2 aromatic protons).

#### Homopolymerization of 4-Hydroxy-3,5-dimethylbenzyl Alcohol

4-Hydroxy-3,5-dimethylbenzyl alcohol (0.40 g, 2.63 mmol) was dissolved in 5.3 mL 5N aqueous NaOH. Benzene (5.3 mL) and TBAH (0.05 g, 0.13 mmol) were added. The reaction mixture was stirred at  $25^\circ\text{C}$  in the presence of air for 24 h. The reaction was quenched by adding cold 1.5 N HCl. The benzene layer was separated, and benzene was removed on a rotovapor. The GPC and  $^1\text{H-NMR}$  analyses of the residue indicated that it contains 95% 4,4'-dihydroxy-3,3',5,5'-tetramethyldiphenylmethane and 5% oligomers. The overall conversion of the reaction was 89%.

#### Polymerization of 4-Bromo-2,6-dimethylphenol in the Presence of 4-Hydroxy-3,5-dimethylbenzyl Alcohol

In a typical polymerization, 4-bromo-2,6-dimethylphenol (2.00 g, 9.96 mmol) and 4-hydroxy-3,5-dimethylbenzaldehyde (0.51 g, 3.32 mmol) were dissolved in 17.7 mL 5N aqueous NaOH. Benzene (17.7 mL) and TBAH (0.23 g, 0.66 mmol) were added. The reaction mixture was stirred vigorously at  $25^\circ\text{C}$  in the presence of air for 24 h. The polymerization was quenched by neutralizing the reaction mixture with cold 1.5 N HCl. The benzene layer was separated and precipitated into methanol. The resulting precipitate was filtered and dried in vacuo to yield 1.01 g (84%) PPO-OH.  $M_n$  (GPC) = 20500,  $M_w/M_n$  = 2.18.

The results of the copolymerization experiments are summarized in Table I.

#### Synthesis of Vinylbenzyl Ether of the PPO Polymers

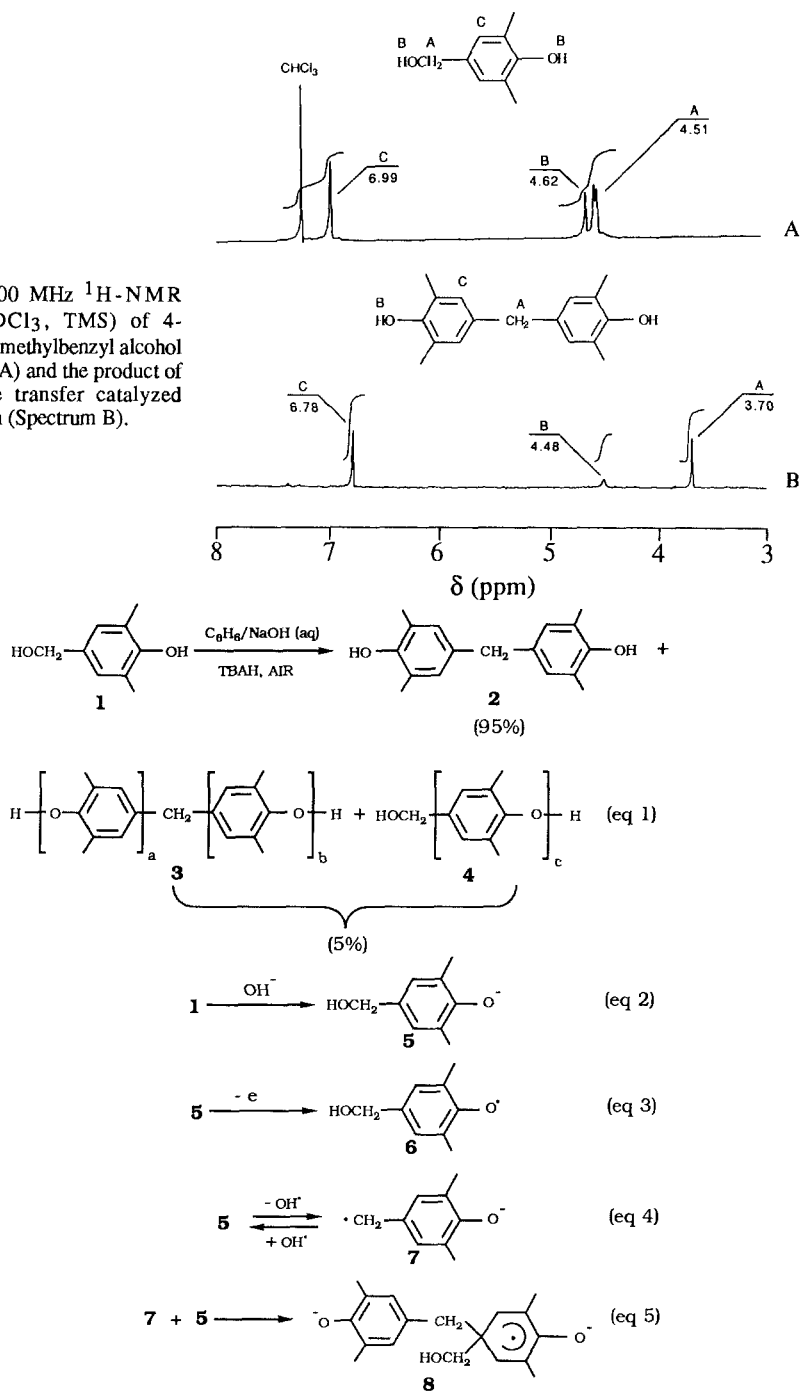
The vinylbenzyl ether of the PPO polymers was synthesized as previously described.<sup>16,17</sup>

## RESULTS AND DISCUSSION

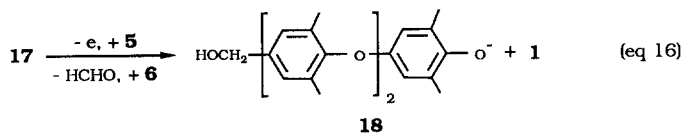
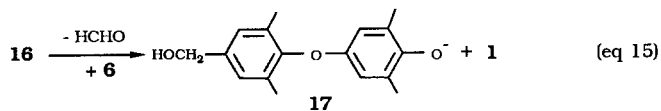
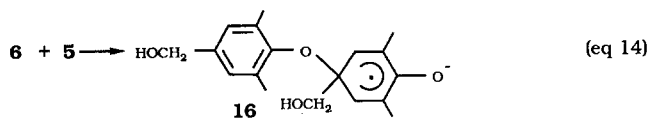
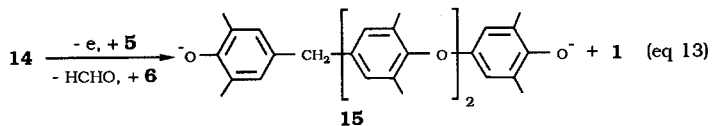
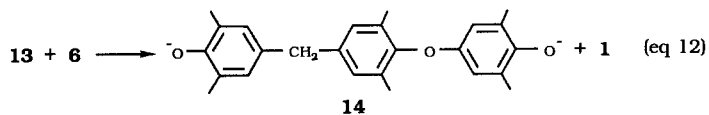
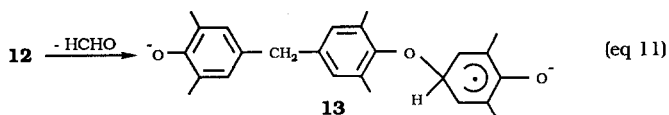
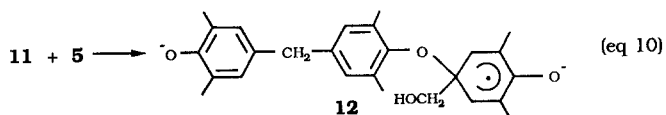
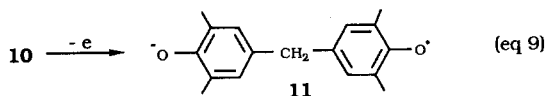
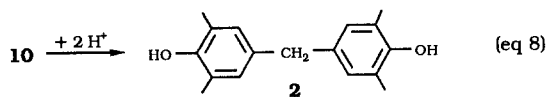
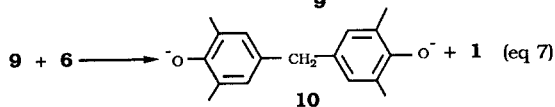
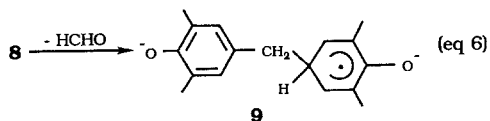
The phase transfer catalyzed homopolymerization of 4-hydroxy-3,5-dimethylbenzyl alcohol (**1**) did not yield a methanol insoluble fraction after 24 h of reaction. The benzene-methanol layer was therefore rotovapored to a residue. The 200 MHz  $^1\text{H-NMR}$  spectrum of the residue is shown as Spectrum B in Figure 1. The corresponding  $^1\text{H-NMR}$  spectrum of **1** before reaction is shown as Spectrum A in Figure 1 for comparison. It is obvious that after reaction the aromatic resonance of **1** was shifted from 6.99 ppm to 6.78 ppm. The corresponding resonance due to  $\text{CH}_2$  group was shifted from 4.51 to 3.70 ppm. Spectrum B corresponds to the structure of 4,4'-dihydroxy-3,3',5,5'-tetramethyldiphenylmethane. The GPC analysis of the reaction product indicates that the residue consists of 95% of 4,4'-dihydroxy-3,3',5,5'-tetramethyldiphenylmethane and 5% higher oligomers. The PTC reaction of **1** is shown in eq 1 from scheme I.

A possible radical-anion mechanism for the PTC reaction of 4-hydroxy-3,5-dimethylbenzyl alcohol (**1**) is outlined in eq 2-16 from Scheme I. Under PTC conditions, **1** is first deprotonated to form its phenolate **5** (eq 2, Scheme I). The phenolate **5** complexed with tetrabutylammonium cation is transferred into the benzene phase, where it is oxidized to its corresponding phenoxy radical **6** (eq 3). The elimination of OH $\cdot$  from the phenolate **5** generates a radical-anion **7** (eq 4), similar to the quinone methide intermediate which was previously proposed in the oxidative polymerization of 2,4,6-trimethylphenol treated with excess manganese oxide.<sup>14</sup> The benzyl radical in the radical-anion **7** attacks the phenolate **5** leading to the radical-anion intermediate **8** (eq 5). The elimination of formaldehyde<sup>14</sup> yields the 4-hydro substituted radical-anion **9** (eq 6).

**Figure 1.** 200 MHz  $^1\text{H-NMR}$  spectra ( $\text{CDCl}_3$ , TMS) of 4-hydroxy-3,5-dimethylbenzyl alcohol (**1**) (Spectrum A) and the product of **1** after phase transfer catalyzed polymerization (Spectrum B).



**Scheme 1.** The proposed radical-anion mechanism for the phase transfer catalyzed polymerization of 4-hydroxy-3,5-dimethylbenzyl alcohol (**1**).



Scheme I (continued)

**9** can not enolize due to its phenolate anion structure. Therefore, the only reasonable elimination is assumed to take place through a radical hydrogen abstraction by the phenoxy radical **6** (eq 7). This reaction leads to the diphenylmethane diphenolate **10**. The quenching of this reaction provides 2 protons to protonate the diphenolate **10** and leads to the neutral 4,4'-dihydroxy-3,3',5,5'-tetramethyldiphenylmethane (**2**) (eq 8). **2** accounts for the 95% of this reaction products. As outlined in eq 9 to 16 from Scheme I the rest of the products consists of 5% oligomers. The oxidation of the diphenolate **10** gives its corresponding phenoxy radical **11** (eq 9). **11** attacks the phenolate **5** (similar to eq 5) leading to the radical anion **12** (eq 10). **12** similarly eliminates formaldehyde (eq 11) and undergoes hydrogen abstraction (eq 12) forming the dimer phenolate **14**. The repetition of eq 10-12 gives the trimer **15** (eq 13). This series of reactions leads to bifunctional oligomers. The other possible reactions that may lead to oligomers are shown in eq 14-16 from Scheme I. These reactions start from the phenoxy radical **6**, which attacks the phenolate **5** (eq 14), eliminating formaldehyde and undergoes hydrogen abstraction (eq 15) to give a monofunctional (referring to the phenol functionality) dimer **17**. The repetition of reactions shown in eq 14 and 15 gives the trimer **18** (eq 16) and higher oligomers.

The phase transfer catalyzed copolymerization experiments of 4-bromo-2,6-dimethylphenol (**19**) with 4-hydroxy-3,5-dimethylbenzyl alcohol (**1**) are summarized in Table I. These copolymerizations were performed with **19/1** molar ratio from 1/1 to 10/1, resulting in polymer yields from 71-95%. The number average molecular weights ( $\bar{M}_n$ ) of the polymers are in the range of 11100 to 27900 g/mol. The relative  $\bar{M}_w/\bar{M}_n$  as determined by GPC calibrated with polystyrene standards increase with increasing **19/1** molar ratio.

Table I. Phase Transfer Catalyzed Polymerization of 4-Bromo-2,6-Dimethylphenol (**19**) in the Presence of 4-Hydroxy-3,5-dimethylbenzyl alcohol (**1**). Phase Transfer Catalyst, TBAH; Polymerization Temperature, 25°C; Polymerization Solvents, Benzene/5N NaOH (aq); Polymerization Time, 24 h.

Exp. No.	<b>19</b> (mmol)	<b>1</b> (mmol)	<b>19/1</b> (mol/mol)	Polymer		
				Yield (%)	$\bar{M}_n$ (GPC) (g/mol)	$\bar{M}_w/\bar{M}_n$
1	1.32	1.32	1/1	71	11100	2.04
2	9.96	3.32	3/1	84	20500	2.18
3	4.98	0.50	10/1	95	27900	2.33

The 200 MHz  $^1\text{H-NMR}$  spectrum of a representative PPO polymer (Sample No. 1, Table I) is presented in Figure 2. As shown in the expanded region, two types of chain ends are observed. The first chain end has a diphenylmethane structure, whose resonance was recorded at 6.94 ppm. It was shifted 0.14

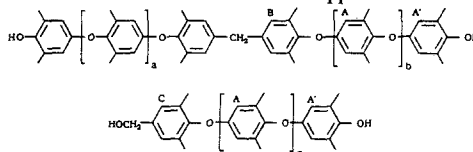
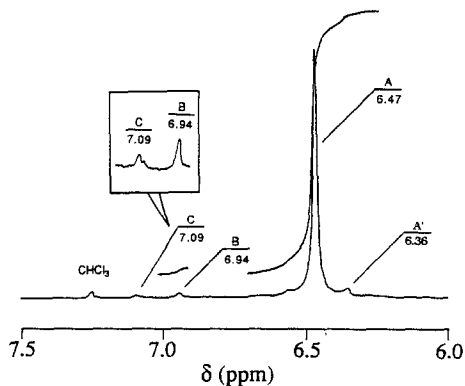
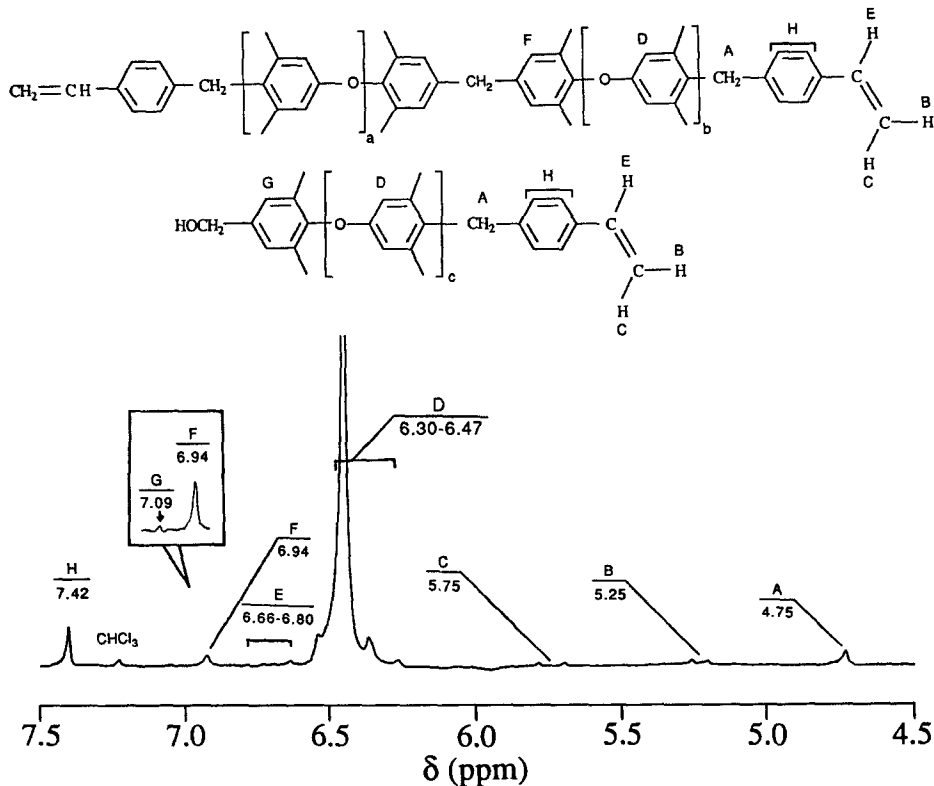


Figure 2. 200 MHz  $^1\text{H-NMR}$  spectrum ( $\text{CDCl}_3$ , TMS) of a representative PPO polymer (Sample No. 1, Table I).



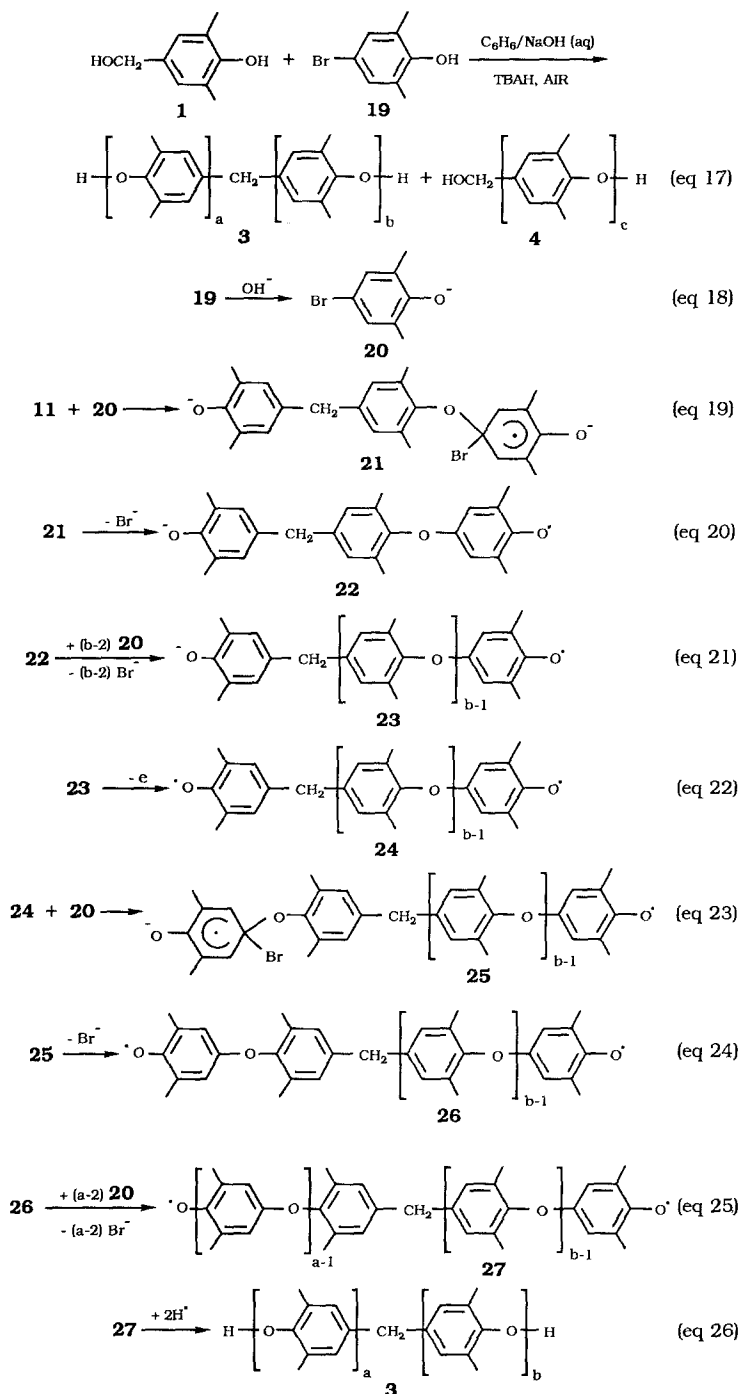
ppm downfield from the monomeric diphenylmethane (Spectrum B, Figure 1). The second chain end contains a 4-hydroxymethyl-2,6-dimethylphenoxy unit (7.09 ppm). It was shifted 0.10 ppm downfield from the original chemical shift of the monomer (6.99 ppm, Spectrum A, Figure 1). The  $M_n$  calculated from the ratio of the integrals of the resonance due to the backbone unit (Signal A, 6.47 ppm, Figure 2) to the resonances due to chain ends (6.94 ppm and 7.09 ppm) is 13000 g/mol. The  $^1\text{H-NMR}$  spectrum indicates that the resulting PPO polymer represents a mixture of PPO-OH and PPO-2OH.

The 200 MHz  $^1\text{H-NMR}$  spectrum of the vinylbenzyl ether derivative of the PPO polymer (Sample No. 1, Table I) is presented in Figure 3. The sum of the integral of the resonances due to chain ends (F and G) is approximately the same as the integral due to proton A and 1/2 that of integral of proton H.

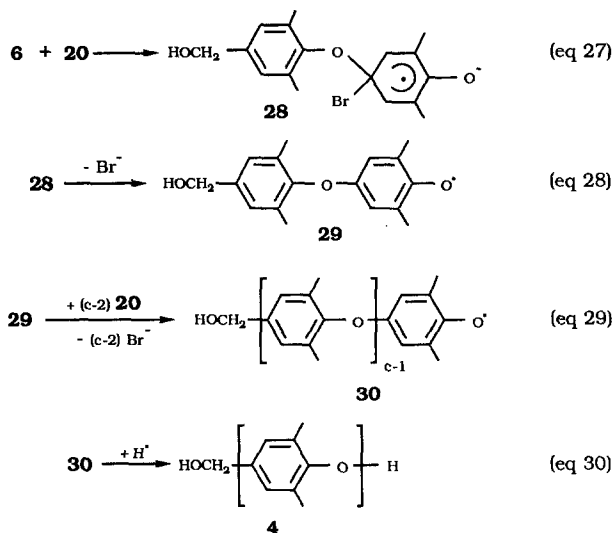


**Figure 3.** 200 MHz  $^1\text{H-NMR}$  spectrum ( $\text{CDCl}_3$ , TMS) of the vinylbenzyl ether of the PPO polymer (Sample No. 1, Table I).

Based on the polymer structure determination, the PTC copolymerization reaction is shown in eq 17 from Scheme II. To account for the polymer structure, a radical-anion mechanism for the polymerization is outlined in eq 18-30 from Scheme II. The deprotonation of 4-bromo-2,6-dimethylphenol (19) is shown in eq 18 leading to its corresponding phenolate 20. The phenoxy radical 11 (eq 9, Scheme I) attacks the 4-bromophenolate 20 giving rise to a radical-anion 21 (eq 19). The subsequent bromide elimination from 21 produces a dimeric phenoxy radical 22 (eq 20). The repeated reactions (eq 19 and 20) generate a polymeric phenoxy radical 23 (eq 21). The phenolate group in 23 can be oxidized to its phenoxy radical 24 (eq 22). The subsequent series of reactions of 24 (eq 23-25) lead to a polymeric biphenoxy radical 27. The termination of 27 generates the PPO-2OH 3 (eq 26). Similar radical-anion reactions of 4-hydroxymethylphenoxy radical 6 (generated by eq 3, Scheme I) are shown in eq 27-30 leading to PPO-OH with 4-hydroxymethyl-2,6-dimethylphenoxy as the non-phenol chain end. The dependence of  $M_n$  on the molar ratio of 19/1 is determined by the relative concentrations of intermediates 11, 6, and 20 in a similar way as that previously discussed.<sup>10</sup>



**Scheme II.** The proposed radical-anion mechanism for the phase transfer catalyzed copolymerization of 4-bromo-2,6-dimethylphenol (19) in the presence of 4-hydroxy-3,5-dimethylbenzyl alcohol (1).



Scheme II (Continued)

**CONCLUSIONS**

The phase transfer catalyzed (PTC) homopolymerization of 4-hydroxy-3,5-dimethylbenzyl alcohol (**1**) resulted in 95% 4,4'-dihydroxy-3,3',5,5'-tetramethyldiphenylmethane and 5% oligomers. The PTC polymerization of 4-bromo-2,6-dimethylphenol (**19**) in the presence of **1** produced a mixture of PPO-2OH and PPO-OH. This polymerization proceeds through a radical-anion mechanism.

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