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Synthesis of α,ω-bis(2,6-dimethylphenol)-poly(2,6-dimethyl-1,4-phenylene oxide) by phase transfer catalyzed polymerization of 4-bromo-2,6-dimethylphenol in the presence of 2,2-di(4-hydroxy-3,5-dimethylphenyl)propane

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SUMMARY

α,ω-Bis(2,6-dimethylphenol)-poly(2,6-dimethyl-1,4-phenylene oxide) (PPO-2OH) was synthesized by the radical-cation phase transfer catalyzed polymerization of 4-bromo-2,6-dimethylphenol (**1**) in the presence of 2,2-di(4-hydroxy-3,5-dimethylphenyl)propane (**2**). Copolymerization experiments were performed by a liquid-liquid two phase, benzene/1.5 N NaOH (aq), phase transfer catalyzed reaction with tetrabutylammonium hydrogen sulfate (TBAH) or tricaprylmethylammonium chloride (Aliquat 336) catalysts. A series of copolymerization experiments were performed with **1**/**2** molar ratios of 4/1, resulting in PPO-2OH with $\overline{M}_n$ in the range of 2200-3200 g/mol. Phase transfer catalyzed etherification of the PPO-2OH chain ends with p-chloromethylstyrene was used to synthesize α,ω-bis(vinylbenzyl ether)s of the PPO-2OH (PPO-2VBE). The chain microstructure and the fuctionality of both PPO-2OH and PPO-2VBE was studied by 200 MHz ^{1}H-NMR spectroscopy.

INTRODUCTION

The synthesis and characterization of α,ω-bis(2,6-dimethylphenol)-poly(2,6-dimethyl-1,4-phenylene oxide) (PPO-2OH) was accomplished only recently.[1-7] PPO-2OH oligomers are of interest since they are precursors for the synthesis of block copolymers,[2] and thermally reactive oligomers.[6]

There are three synthetic procedures available for the synthesis of PPO-2OH. The first method was developed by White.[1] A low molecular weight poly(2,6-dimethyl-1,4-phenylene oxide) with one phenol chain end (PPO-OH) was reacted with 3,3',5,5'-tetramethyl-1,4-diphenoquinone by a radical-radical mechanism. Heitz et al.[4,5] have developed the second method which is based on the electrophilic condensation reaction of two PPO-OH molecules via their phenyl end group with formaldehyde. This reaction was catalyzed by either Brϕnsted or Lewis acids. The third procedure consists of radical-radical oxidative copolymerization of 2,6-dimethylphenol with 2,2'-di(4-hydroxy-3,5-dimethylphenyl)propane. Two variants of this synthetic procedure were described in the literature. The first one was by Heitz et al.[3-5] In this method the molecular weight and the functionality of PPO-2OH are determined during the propagation step. In the second method by Nava and Percec,[6] the molecular weight and the functionality of PPO-2OH were controlled by the redistribution reactions.

Previous experiments from our laboratory have demonstrated that phase transfer catalyzed polymerization of 4-bromo-2,6-dimethylphenol in the presence of either 2,4,6-trimethylphenol or 4-tert-butyl-2,6-dimethylphenol can be used to synthesize perfectly monofunctional PPO-OH with controlled molecular weight.[8]

The goal of this paper is to describe a novel synthetic procedure for the synthesis of PPO-2OH oligomers. It consists of the phase transfer catalyzed polymerization of 4-

bromo-2,6-dimethylphenol in the presence of 2,2-di(4-hydroxy-3,5-dimethylphenyl)propane. This polymerization proceeds through a radical-anion mechanism. The bifunctionality of the resulting PPO-OH was determined by ^{1}H-NMR spectroscopy performed on PPO-2OH and on the α,ω-bis(vinylbenzyl) ethers of PPO-2OH.

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), tricaprylmethylammonium chloride (Aliquat 336, Aldrich), p-chloromethylstyrene (Seimi Chemical, Kanagawa, Japan), and all the other reagents were used as received.

Techniques

200 MHz ^{1}H-NMR spectra (δ, ppm) were recorded on a Varian XL-200 spectrometer. All spectra were recorded in $CDCl_3$ with TMS as internal standard. GPC measurements were performed on a Perkin-Elmer series 10 LC instrument equipped with an LC-100 column oven, 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°C), a set of PL-gel colums (500 and 10^4 Å), and a calibration plot constructed with polystyrene standards (Supelco).

2,2-Di(4-hydroxy-3,5-dimethylphenyl)propane (2)

2,2-Di(4-hydroxy-3,5-dimethylphenyl)propane was prepared following a literature procedure.[6,9] White crystals were obtained by recrystallization from aqueous methanol and benzene, mp. 164-165°C. Purity (HPLC): >99.9%. ^{1}H-NMR: 1.58 (s, $-C(C\underline{H}_3)_2-$, 6H), 2.18 (s, $Ph-C\underline{H}_3$,12H), 4.47 (s, $-Ph-O\underline{H}$, 2H), 6.82 (s, $Ph-\underline{H}$, 4H).

Phase Transfer Catalyzed Polymerization of 4-Bromo-2,6-dimethylphenol (1) in the presence of 2,2-Di(4-hydroxy-3,5-dimethylphenyl)propane (2)

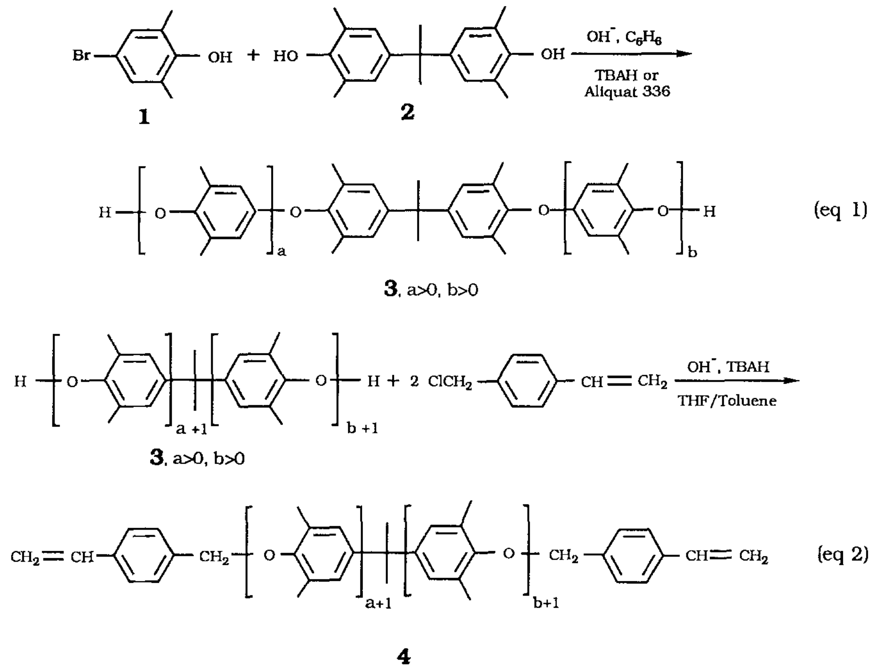
In a typical polymerization experiment, 4-bromo-2,6-dimethylphenol (5.00 g, 24.9 mmol) was added to a solution of 2,2-di(4-hydroxy-3,5-dimethylphenyl)propane (1.77 g, 6.22 mol) in 50 mL 1.5 N aqueous NaOH. To the reaction mixture, 50 mL benzene and TBAH (0.422 g, 1.24 mmol) were added. The reaction was stirred for 24 h at 25°C in the presence of air. The polymerization was quenched by neutralizing with cold 1.5 N HCl solution. The benzene layer was precipitated into methanol. The precipitate was filtered and dried in vacuo to yield 1.177 g (25%) PPO-2OH (**3**). $\overline{M}_n$ (GPC): 2700 g/mol, $\overline{M}_w/\overline{M}_n$=1.43. The results of the polymerization experiments are listed in Table I.

Synthesis of α,ω-Bis(Vinylbenzyl Ether) of Poly(2,6-Dimethyl-1,4-Phenylene Oxide) (PPO-2VBE)

PPO-2VBE was prepared by a method similar to that used in the synthesis of PPO-VBE.[8,10] PPO-2OH (**3**, $\overline{M}_n$=3200 g/mol, $\overline{M}_w/\overline{M}_n$=1.41, 0.20 g, 1.24 X$10^{-4}$ mol phenolic -OH) was dissolved in 4 mL toluene and 4 mL tetrahydrofuran. Dry nitrogen was bubbled to remove air-oxygen. p-Chloromethylstyrene (0.19 g, 1.24X10^{-3} mol) and 0.40 mL 3N aqueous NaOH were added. The content was deaerated by a stream of nitrogen for 1 h, and finally TBAH (0.042 g, 1.24X10^{-4} mol) was added. The reaction mixture was stirred for 6 h at 25°C, and then acidified with excess 1.5 N HCl solution. The organic layer was precipitated into methanol. The precipitate was filtered and dried in vacuo to yield 0.19 g (87%) PPO-2VBE. $\overline{M}_n$ (GPC): 3900 g/mol, $\overline{M}_w/\overline{M}_n$ = 1.44.

RESULTS AND DISCUSSION

The phase transfer catalyzed polymerization of 4-bromo-2,6-dimethylphenol (**1**) in the presence of 2,2-di(4-hydroxy-3,5-dimethylphenyl)propane (**2**) is outlined in reaction 1 from Scheme I. The polymerization results are listed in Table I. Polymerization experiments were performed with **1**/**2** molar ratios of 4/1, and by using either TBAH or Aliquat 336 as phase transfer catalyst. The obtained polymers have number average molecular weight ($\overline{M}_n$) in the range of 2200 to 3200. The polymer yield was 14 to 25% presumably due to the fact that lower molecular weight PPO-2OH oligomers are soluble in methanol and therefore are lost during the precipitation process.[6]



Scheme I. The phase transfer catalyzed synthesis of PPO-2OH and PPO-2VBE.

Table I. Phase Transfer Catalyzed Polymerization of 4-Bromo-2,6-Dimethylphenol (**1**) in the Presence of 2,2-Di(4-Hydroxy-3,5-Dimethylphenyl)Propane (**2**). Polymerization Temperature, 25°C; Polymerization Solvents, Benzene/1.5N NaOH (aq).

Exp. No.	**1** (mmol)	**2** (mmol)	**1**/**2** (mol/mol)	Phase Transfer Catalyst	Reaction Time (h)	Polymer Yield (%)	$\overline{M}_n$ (GPC) (g/mol)	$\overline{M}_w/\overline{M}_n$
1	24.9	6.22	4/1	TBAH	24	25	2700	1.43
2	24.9	6.22	4/1	TBAH	12	17	3200	1.41
3	4.98	1.24	4/1	TBAH	24	16	2600	1.22
4	4.98	1.24	4/1	Aliquat 336[a]	24	19	2200	1.22
5	4.98	1.24	4/1	TBAH	12	14	3000	1.41

a) tricaprylmethylammonium chloride.

The structure of the PPO-2OH oligomers is determined by 200 MHz ^{1}H-NMR spectroscopy. For the polymerization performed for 12 h (Sample No. 2 and 5, Table I), the polymer contains both 4-bromo-2,6-dimethylphenoxy[8,10] chain ended monofunctional PPO-OH and bifunctional PPO-2OH. However, the polymers prepared by a 24 h polymerization exhibit only resonances due to PPO-2OH. A typical 200 MHz ^{1}H-NMR spectrum of PPO-2OH (Sample No. 3, Table I) is shown in Figure 1. The protonic assignments are printed on the figure. A detailed discussion on their assignments was presented elsewhere.[6] This spectrum indicates two types of 2,2-di(4-hydroxy-3,5-dimethylphenyl)propane (**2**) derived structural units. The unit located in the polymer backbone exhibits its aromatic resonance at 6.97 ppm, but the **2** derived terminal unit gives rise to an aromatic resonance of lower intensity at 6.87 ppm. No 4-bromo-2,6-dimethylphenoxy group (7.18 ppm)[8,10] was observed in this ^{1}H-NMR spectrum. The $\overline{M}_n$ of the PPO-2OH can be determined from the integral ratio of resonances due to protons I + J to those due to K + L.[6] The $\overline{M}_n$ calculated from the ^{1}H-NMR spectrum of sample No. 3 from Table I is 2300 g/mol, while the $\overline{M}_n$ determined by GPC is 2600 g/mol.

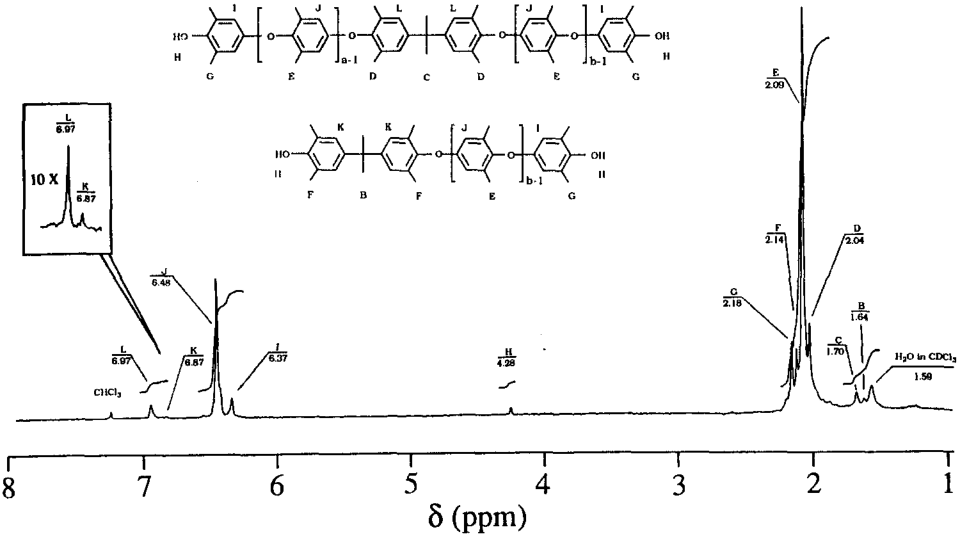


Figure 1. 200 MHz ^{1}H-NMR spectrum (CDCl$_3$, TMS) of PPO-2OH (Sample No.3, Table I).

In order to determine the chain ends functionality of the PPO-2OH, the phenol chain ends were etherified under phase transfer catalyzed conditions with p-chloromethylstyrene (eq 2, Scheme I). A quantitative transformation of PPO-2OH into PPO-2VBE can be accomplished by this reaction.[6,8,10] The 200 MHz ^{1}H-NMR spectrum of the resulting PPO-2VBE is shown in Figure 2. The resonances due to the vinylbenzyl ether units and the polymer backbone are clearly observed. Within the experimental error of ^{1}H-NMR technique, the resonance due to the S protons (8 each PPO-2VBE molecule) in the vinylbenzylether group is twice the integral of the L protons (4 protons each PPO-2OH molecule) in the **2** derived unit. Therefore, the PPO-2OH synthesized by the phase transfer catalyzed copolymerization is indeed perfectly bifunctional.

Figure 3 shows the GPC traces of the PPO-2OH oligomers and of the PPO-2VBE derivative. Curve A is the chromatogram of a PPO-2OH of $\overline{M}_n$ = 2200 g/mol, $\overline{M}_w/\overline{M}_n$ =

1.22. Curve B represents the chromatogram of a PPO-2OH sample synthesized under different experimental conditions (Sample No. 3, Table I). The GPC trace of the vinylbenzyl ether synthesized from the PPO-2OH (Curve B) is presented as Curve C. The PPO-2VBE possesses a higher molecular weight than the parent PPO-2OH due to the added vinylbenzyl ether chain ends.

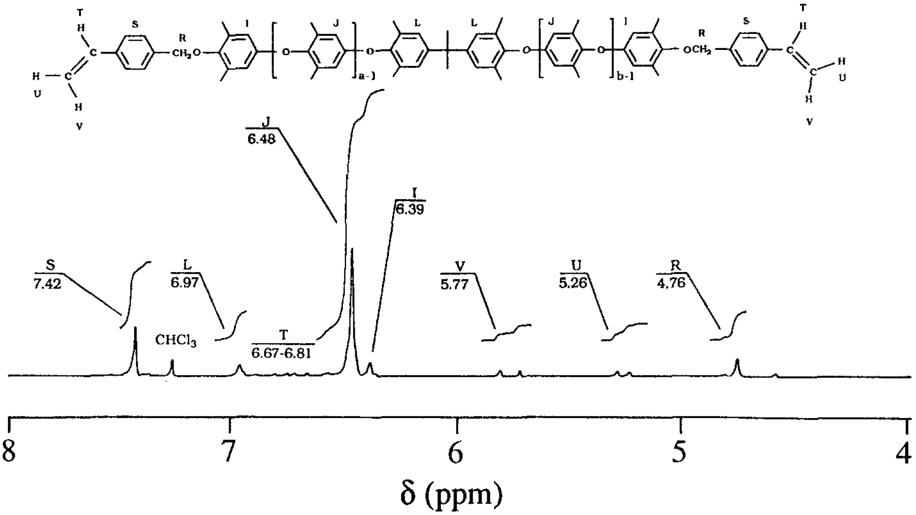


Figure 2. 200 MHz ^{1}H-NMR spectrum (CDCl$_3$, TMS) of PPO-2VBE (synthesized from Sample No. 3, Table I) (an expansion of 4-8 ppm region).

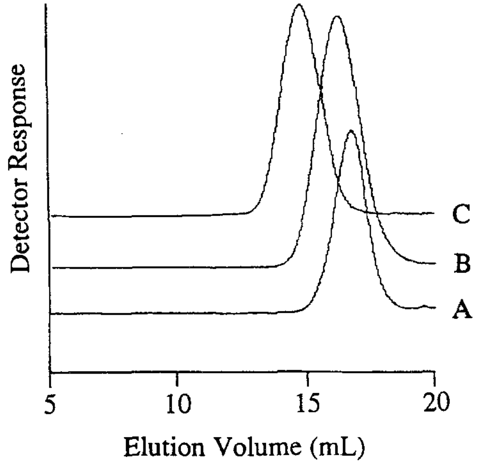
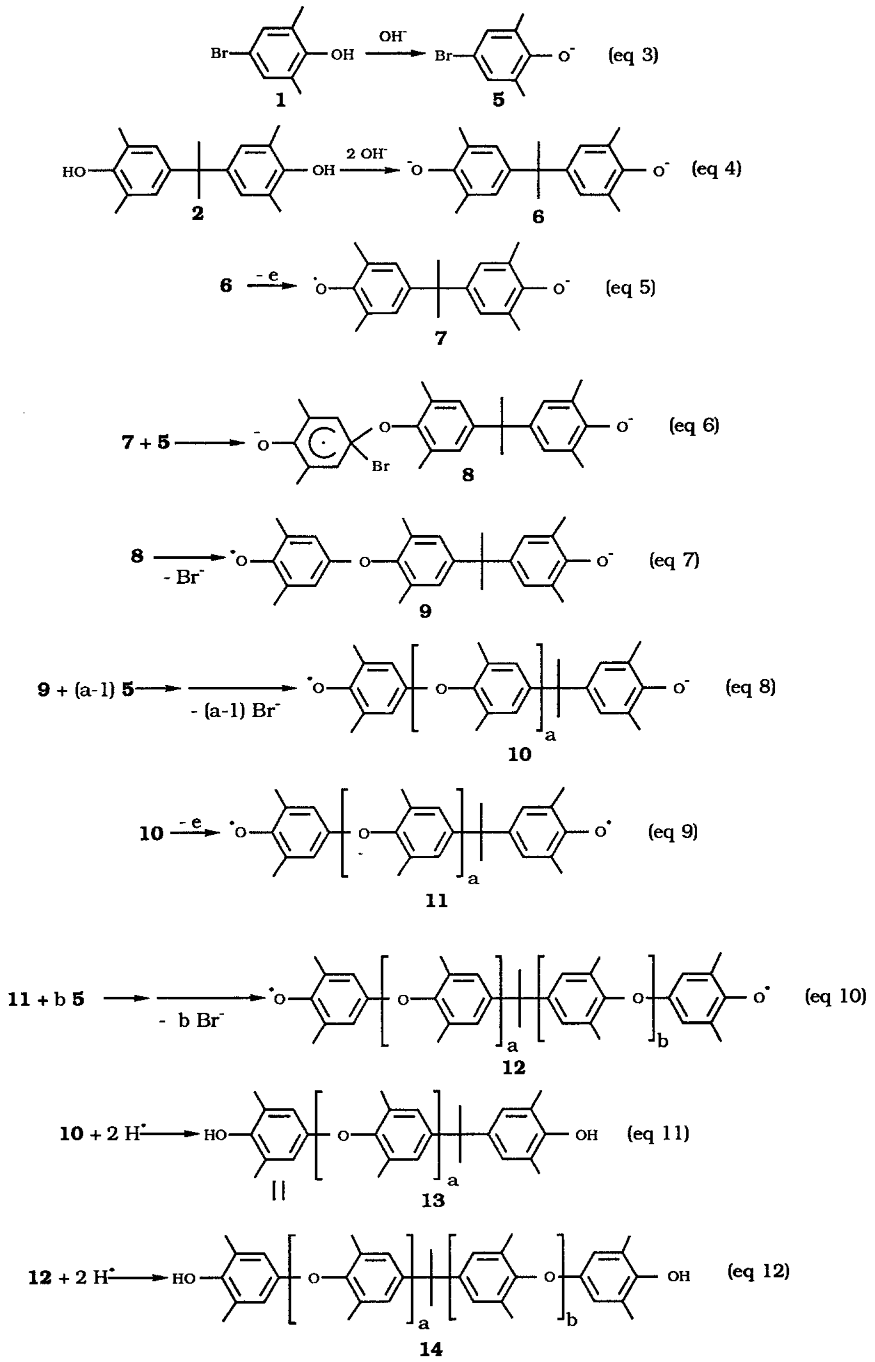
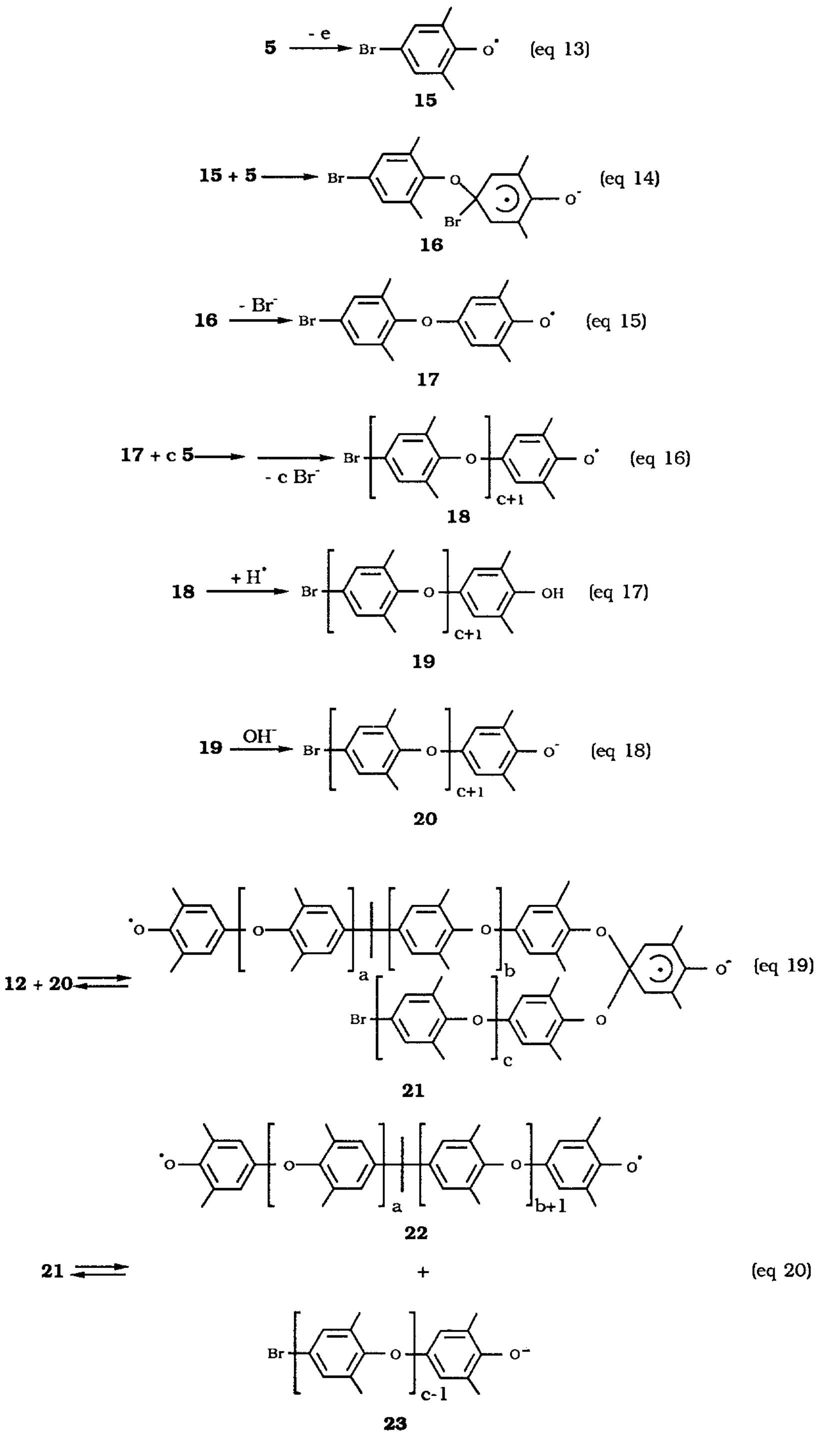


Figure 3. GPC traces of PPO-2OH and PPO-2VBE: A) PPO-2OH (Sample No. 4, Table I); B) PPO-2OH (Sample No. 3, Table I); C) PPO-2VBE (synthesized from Sample No. 3, Table I).

Based on these experimental results, we propose the radical-anion mechanism of polymerization from Scheme II. Eq 3 and 4 present the deprotonation reactions of 4-bromo-2,6-dimethylphenol (**1**) and 2,2-di(4-hydroxy-3,5-dimethylphenyl)propane (**2**) leading to the the corresponding phenolates **5** and **6**. The phenolates **5** and **6** are transfered into organic phase as the corresponding onium phenolates with tetrabutylammonium or tricaprylmethylammonium ions as their counter-anions. The first step of the polymerization is the oxidation of the phenolate group in the bisphenolate **6** to the corresponding phenoxy



Scheme II. The radical-anion mechanism for the phase transfer catalyzed polymerization of 4-bromo-2,6-dimethylphenol in the presence of 2,2-di(4-hydroxy-3,5-dimethylphenyl)propane.



Scheme II (Continued).

radical (eq 5). The phenoxy radical **7** then attacks the 4-position of the 4-bromo-2,6-dimethylphenolate (**5**) (eq 6) and the radical anion intermediate **8** releases Br^- to form a dimeric phenoxy radical **9** (eq 7). The radical **9** will subsequently repeat these reactions (eq 6 and 7) as shown in eq 8 to form a polymeric phenoxy radical **10**. The phenolate end group in **10** can be similarly oxidized (eq 9), and participates in repeated propagation leading to polymeric diradicals **12** (eq 10). The termination of **10** yields polymer **13** which has a **2** derived terminal unit. Figure 1 demonstrates the presence of this polymer structure in small percentage. The termination of **12** produces the polymer structure **14** with **2** derived units located within the backbone. Figure 1 demonstrates that structure **14** predominates in the PPO-2OH polymers.

Due to the lower oxidation potential of bisphenolate **6** than 4-bromo-2,6-dimethylphenolate (**5**), bisphenolate **6** is more favorably oxidized than **5**. However, the oxidation of **5** (eq 13) and the subsequent propagation reactions (eq 14, 15, 16) represent an important series of side reactions. These side reactions lead to monofunctional PPO-OH (eq 17). This reaction has been observed from the polymers prepared by a short polymerization experiment (12 h). However, as determined by ^{1}H-NMR spectroscopy (Figure 1) the PPO-2OH polymers synthesized by a 24 h polymerization do not exhibit resonances due PPO-OH. Therefore, although PPO-OH is initially generated, the subsequent redistribution reactions (eq 19 and 20) transform the PPO-OH to high molecular PPO-2OH and low molecular weight PPO-OH. Since the low molecular weight oligomers of PPO-OH are soluble in methanol,[6] they are lost during the purification process. Therefore, when this reaction is performed for 24 h, it generates perfectly bifunctional PPO-2OH.

CONCLUSIONS

The synthesis of perfectly bifunctional PPO-2OH has be successfully accomplished by a 24 h phase transfer catalyzed polymerization of 4-bromo-2,6-dimethylphenol in the presence of 2,2-di(4-hydroxy-3,5-dimethylphenyl)propane. The polymer generated after 12 h contains both bifunctional PPO-2OH and monofunctional PPO-OH. This polymerization proceeds by the radical-anion mechanism which was advanced in previuos publications.[8, 11-13]

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