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Phase transfer catalyzed polymerization of 4-bromo-2,6-dimethylphenol in the presence of a terminating comonomer phenol: 2,4,6-tri-*tert*-butylphenol or 4-bromo-2,6-di-*tert*-butylphenol

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SUMMARY

This paper describes the phase transfer catalyzed (PTC) polymerization of 4-bromo-2,6-dimethylphenol (1) in the presence 2,4,6-tri-tert-butylphenol (2) or 4-bromo-2,6-di-tert-butylphenol (4). The polymerization of 1 in the presence of 2 at a 1/2 molar ratio of 3/1 led to poly(2,6-dimethyl-1,4-phenylene oxide) (PPO) with $\overline{M}_n$ of 13400 g/mol at a yield of 85%. In contrast, the polymerization of 1 in the presence of 4 at 1/4 molar ratios of 5/1 and 10/1 did not produce any methanol insoluble PPO fraction when 4 was added at the beginning of the polymerization. However, PPO with $\overline{M}_n$ = 1600 to 2400 g/mol were obtained when 4 was added to the polymerization system after 0.5 h and respectively 2.0 h after the homopolymerization of 1 was started. A radical-anion mechanism is proposed to account for these polymerization results.

INTRODUCTION

There are two well-established approaches to the synthesis of poly(2,6-dimethyl-1,4-phenylene oxide) (PPO) polymers. The first one consists of the polymerization of 2,6-dimethylphenol in the presence of a copper-amine complex catalyst.[1-8] A radical-radical coupling mechanism is considered for this polymerization. However, Challa and co-workers have recently proposed an alternative ionic mechanism for this polymerization.[9-13] The second synthesis is based on a radical-anion polymerization of 4-bromo-2,6-dimethylphenol under both phase transfer catalyzed (PTC) and non-phase transfer catalyzed two phase reaction conditions.[1-5,7,14] The PPO polymers synthesized by the radical-anion polymerization contain only one 2,6-dimethylphenol group per polymer molecule (PPO-OH), and are therefore ideal as precursors for chain ended functional PPO.[15,16]

Previous results from our laboratory have demonstrated that the 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 is a novel technique to synthesize PPO with one phenol chain end and with controllable molecular weights.[17] The synthetic procedure and the mechanism for controlling molecular weights were described in detail.[17] 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.[18] The PTC polymerization of 4-bromo-2,6-dimethylphenol in the presence of 4-hydroxy-3,5-dimethylbenzyl alcohol was reported recently to yield a mixture of monofunctional (PPO-OH) and bifunctional (PPO-2OH) PPO.[19] However, there are no reported studies on the radical-anion polymerization of 4-bromo-2,6-dimethylphenol in the presence of a terminating phenol.

The first goal of this paper is to describe the phase transfer catalyzed polymerization of 4-bromo-2,6-dimethylphenol in the presence of a 4-substituted-2,6-di-tert-butylphenol: 2,4,6-tri-tert-butylphenol or 4-bromo-2,6-di-tert-butylphenol. The second goal is to discuss the mechanisms of these PTC polymerizations.

EXPERIMENTAL

Materials

4-Bromo-2,6-dimethylphenol (97%, Aldrich) was recrystallized from petroleum ether. 2,4,6-Tri-tert-butylphenol (96%, Aldrich), tetrabutylammonium hydrogen sulfate (TBAH) (97%, Aldrich), 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 the internal standard. Gel Permeation Chromatography (GPC) measurements were performed on a Perkin-Elmer series 10 LC instrument equipped with an LC-100 column

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*To whom offprint requests should be sent 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°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 performance liquid chromatography (HPLC)/GPC using a 100 Å PL-gel column.

Synthesis of 4-Bromo-2,6-di-tert-butylphenol (4)

2,6-Di-tert-butylphenol (10.30 g, 50 mmol) was dissolved in 50 mL glacial acetic acid. Bromine (7.90 g, 50 mmol) was added dropwise to the solution under vigorous stirring. The reaction mixture was stirred for 1 h. Water (100 mL) was added to the solution, followed by extraction 3 times with chloroform. The chloroform solution was washed with 10% aqueous sodium bicarbonate, then water, and dried over anhydrous sodium sulfate. The resulting solution was filtered, the solvent was evaporated and the product was recrystallized from methanol/water (1/10, v/v) to yield 8.42 g (59%) of **4**. Purity: 99.5%, mp 82-83°C (Lit.[20] mp 83-83.5°C). ^{1}H-NMR: 1.42 (s, 18H, $C(C\underline{H}_3)_3$), 5.00 (s, 1H, Ph-O$\underline{H}$), 7.14 (s, 2H, 2 aromatic protons).

Polymerization of 4-Bromo-2,6-dimethylphenol in the Presence of a Comonomer Phenol

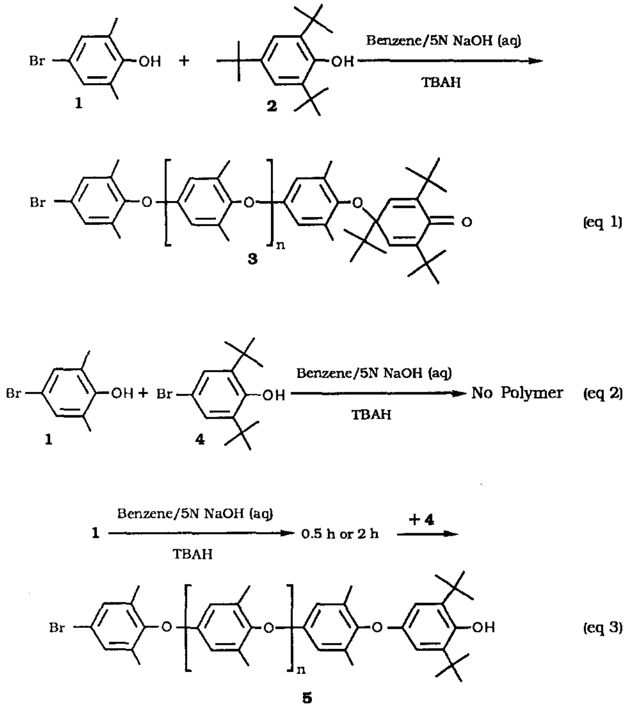
In a typical polymerization, 4-bromo-2,6-dimethylphenol (2.00 g, 9.96 mmol) and 2,4,6-tri-tert-butylphenol (0.87 g, 3.32 mmol) were dissolved in 18.4 mL 5N aqueous NaOH. Benzene (18.4 mL) and TBAH (0.17 g, 0.50 mmol) were added. The reaction mixture was stirred vigorously at 25 °C in the presence of 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 1.14 g (85%) PPO. $\overline{M}_n$ (GPC) = 13400, $\overline{M}_w/\overline{M}_n = 2.96$.

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

RESULTS AND DISCUSSION

4-Bromo-2,6-dimethylphenol was polymerized in the presence of two types of 4-substituted-2,6-di-tert-butylphenols: 2,4,6-tri-tert-butylphenol (**2**) and 4-bromo-2,6-di-tert-butylphenol (**4**). These reactions are illustrated in eq 1 to 3 from Scheme I. The polymerization results are listed in Table I.

For the polymerization of bromo-2,6-dimethylphenol (**1**) in the presence of 2,4,6-tri-tert-butylphenol (**2**) (eq 1, Scheme I), a 1/2 molar ratio of 3/1 resulted in a PPO with $\overline{M}_n = 13400$ and $\overline{M}_w/\overline{M}_n = 2.96$ (Exp. No. 1, Table I).



Scheme I. Phase transfer catalyzed polymerizations of **1** in the presence of 4-substituted-2,6-di-tert-butylphenol (**2** and **4**).

Table I. Phase Transfer Catalyzed Polymerization of 4-Bromo-2,6-Dimethylphenol (**1**) in the Presence of 2,4,6-Tri-tert-Butylphenol (**2**) or 4-Bromo-2,6-Di-tert-Butylphenol (**4**). Phase Transfer Catalyst, TBAH; Polymerization Temperature, 25°C; Polymerization Solvents, Benzene/5N NaOH (aq); Polymerization Time, 24 h.

Exp. No.	**1** (mmol)	Comonomer/ (mmol)	1/Comonomer (mol/mol)	Polymer		
				Yield (%)	$\overline{M}_n$ (GPC) (g/mol)	$\overline{M}_w/\overline{M}_n$
1	9.96	**2**/3.31	3/1	85	13400	2.96
2	4.98	**4**/1.00	5/1	0[a]	-	-
3	4.98	**4**/0.50	10/1	0[a]	-	-
4	9.96	**4**/1.00	10/1	0[a]	-	-
5	9.96	**4**/1.00[b]	10/1	26	1600	2.10
6	9.96	**4**/1.00[c]	10/1	42	2400	1.66

a) No methanol insoluble polymer was obtained, i.e. no PPO polymer with $\overline{M}n>800$ g/mol[8] was produced.
b) **4** was added 0.5 h after the homopolymerization of **1** was started.
c) **4** was added 2.0 h after the homopolymerization of **1** was started.

The 200 MHz ^{1}H-NMR spectrum of the resulting PPO polymer (Sample No. 1, Table I) is shown in Figure 1. The resonances due to the 27 protons of the tert-butyl groups are observed at 1.23-1.45 ppm. From the integrals of the resonance due to the tert-butyl protons (1.23-1.45 ppm) and that due to the backbone PPO repeating unit (2.09 ppm), the number average molecular weight ($\overline{M}_n$) is calculated to be about 11000 g/mol. The proton resonance due to the 4-bromo-2,6-dimethylphenoxy chain end was barely observed at 7.10 ppm.

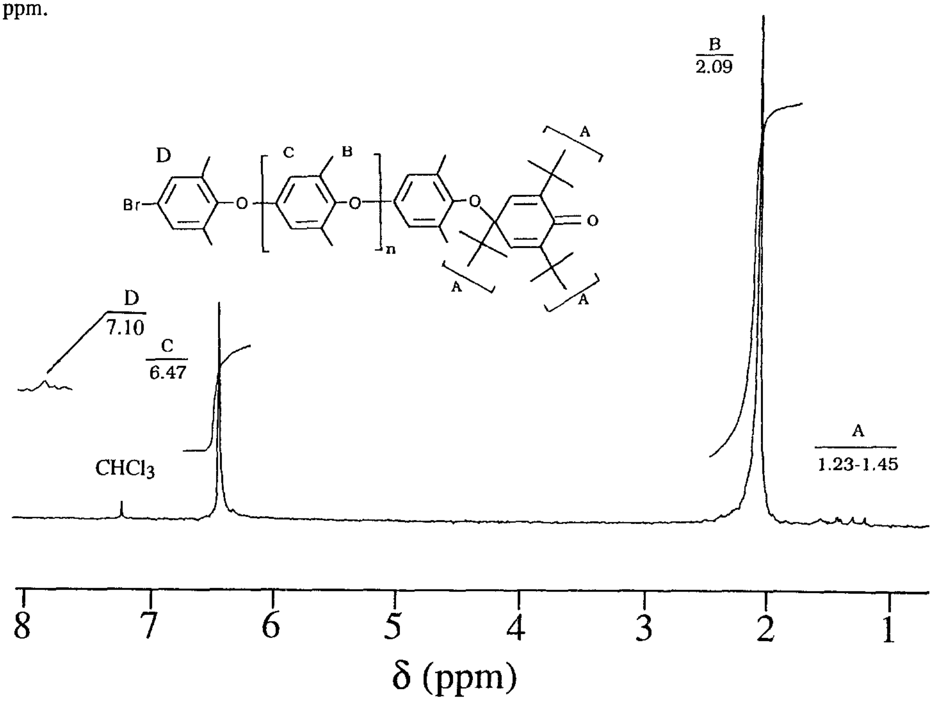


Figure 1. 200 MHz ^{1}H-NMR spectrum ($CDCl_3$, TMS) of polymer (Sample No. 1, Table I).

The radical-anion mechanism suggested for the phase transfer catalyzed polymerization of **1** in the presence of **2** is outlined in eq 4-14 from Scheme II. Because 2,4,6-tri-tert-butylphenol (**2**) is only soluble in organic phase,[21] it is deprotonated in the organic phase by either 4-bromo-2,6-dimethylphenolate (**9**) or OH^{-} [22] to form the phenolate **6**. (eq 4). The oxidation of phenolate **6** generates its corresponding phenoxy radical **7** (eq 5). This 2,4,6-tri-tert-butylphenoxy radical (**7**) has been shown to couple with other phenoxy radicals,[23,24] with nitrogen dioxide radical,[25] and with neutral molecules such as acetic acid and methanol.[26] The radical **7** has been used as an initiator for the non-phase transfer catalyzed polymerization of 4-bromo-2,6-dimethylphenol,[21] 4-bromo-2,6-disubstituted phenols,[27] and for the redistribution reactions of phenol dimers. [28] Radical **7** can initiate the polymerization by proton abstraction from the monomers' phenolic OH.[21,27] However, this reaction does not occur under phase transfer catalyzed reaction conditions due to the absence of free phenol monomer (**1**). The attack of 2,4,6-tri-tert-butylphenoxy radical (**7**) on the 2,4,6-tri-tert-butylphenolate (**6**) (eq 6) does not occur due to steric hindrance both at the phenoxy radical site in **7** (caused by two bulky tert-butyl groups at the ortho positions) and at the 4-position in **6** by the 4-tert-butyl group in the phenolate **6**. Under the PTC polymerization conditions, 4-bromo-2,6-dimethylphenol (**1**) is deprotonated to its phenolate **9** (eq 7). The subsequent oxidation of **9** generates its phenoxy radical **10** (eq 8). The homopolymerization of 4-bromo-2,6-dimethylphenol (**1**) by a radical-anion reaction takes place by the attack of the phenoxy radical **10** on the phenolate **9** (eq 9). This attack leads to the radical-anion intermediate **11** (eq 9). The bromide elimination from **11** yields the dimer phenoxy radical **12** (eq 10). The repeated reactions shown in eq 9 and 10 produce the polymeric phenoxy radical **13** (eq 11). The attack of 2,4,6-tri-tert-butylphenoxy radical (**7**) on 4-bromo-2,6-dimethylphenolate (**9**) (eq 12) does not occur due to the steric hindrance of the phenoxy radical **7**. Therefore, the only possible reaction for 2,4,6-tri-tert-butylphenol (**2**) derived species is a radical-anion reaction of a growing polymeric phenoxy radical **13** at the 4-position of the 2,4,6-tri-tert-butylphenolate (**6**) (eq 13), leading to 4-tert-butyl radical-anion **15**. Due to the steric hindrance by the bulky 4-tert-butyl group this reaction is not kinetically favored and therefore, **15** dissociates back to its starting radical and anion. **15** is also incapable of eliminating 4-tert-butyl group similar to the bromide elimination (eq 10) to achieve the benzene ring conjugation. The oxidation of **15** produces the quinol ether structure **16** (eq 14).

Since the polymerization of **1** in the presence of **2** gives PPO with $\overline{M}_n$ of 13400 g/mol, chain termination by the 2,4,6-tri-tert-butylphenoxy radical **7** is kinetically unfavorable due to the high steric hindrance at the 4-position caused by the 4-tert-butyl group.

The polymerization of **1** in the presence of **4** is presented in eq 2 and 3 from Scheme I. Two different experimental approaches have been taken. The first approach is a copolymerization method in which **1** and **4** were both added simultaneously at the beginning of the polymerization (eq 2, Scheme I). These polymerization experiments failed to produce any methanol insoluble PPO (usually $\overline{M}_n$ > 800 g/mol[8]) (Exp. No. 2-4, Table I). The solvent of the benzene layer separated from this polymerization was removed by evaporation yielding a residue. A typical 200 MHz ^{1}H-NMR spectrum of the residue (from Exp. No. 2, Table I) is shown in Figure 2. From the resonances of high intensity at 2.21 and 7.10 ppm and the GPC

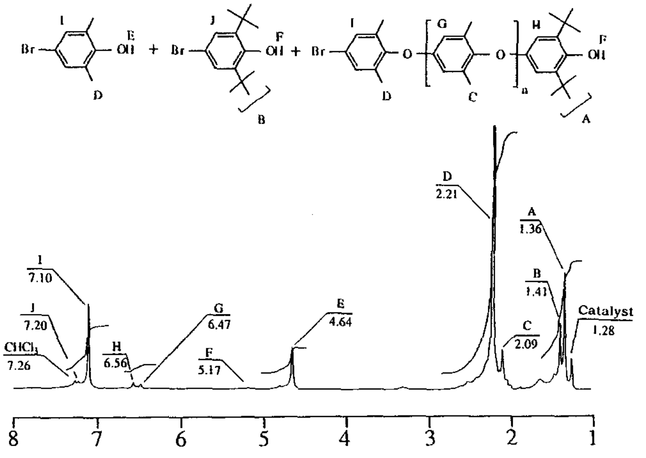
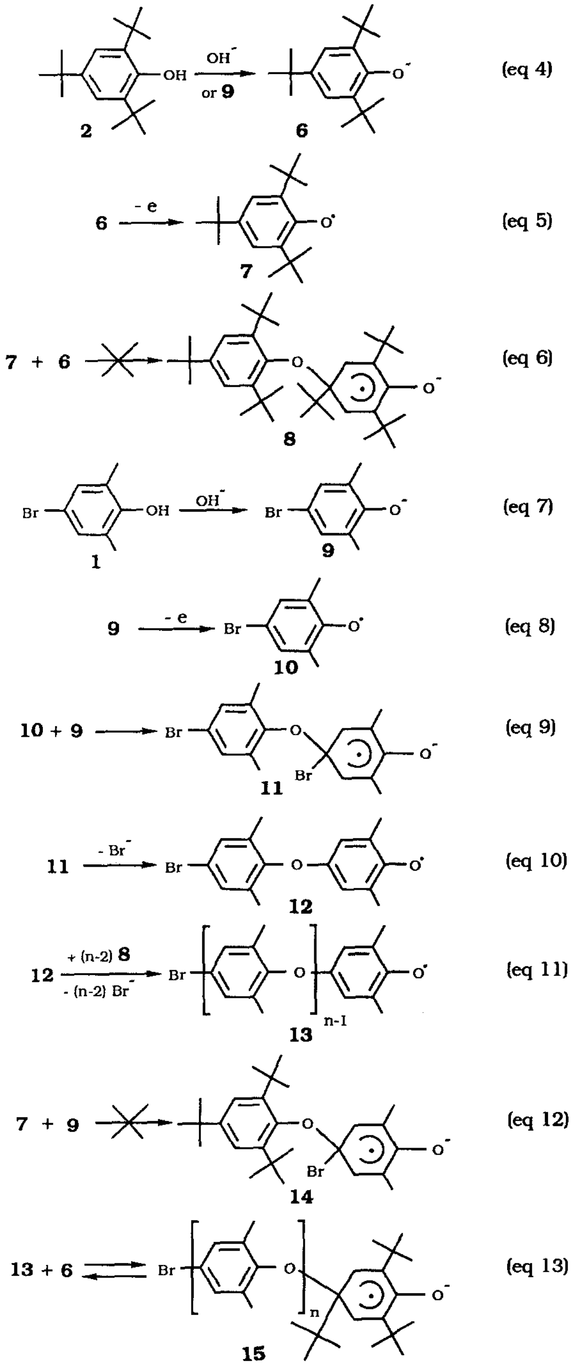
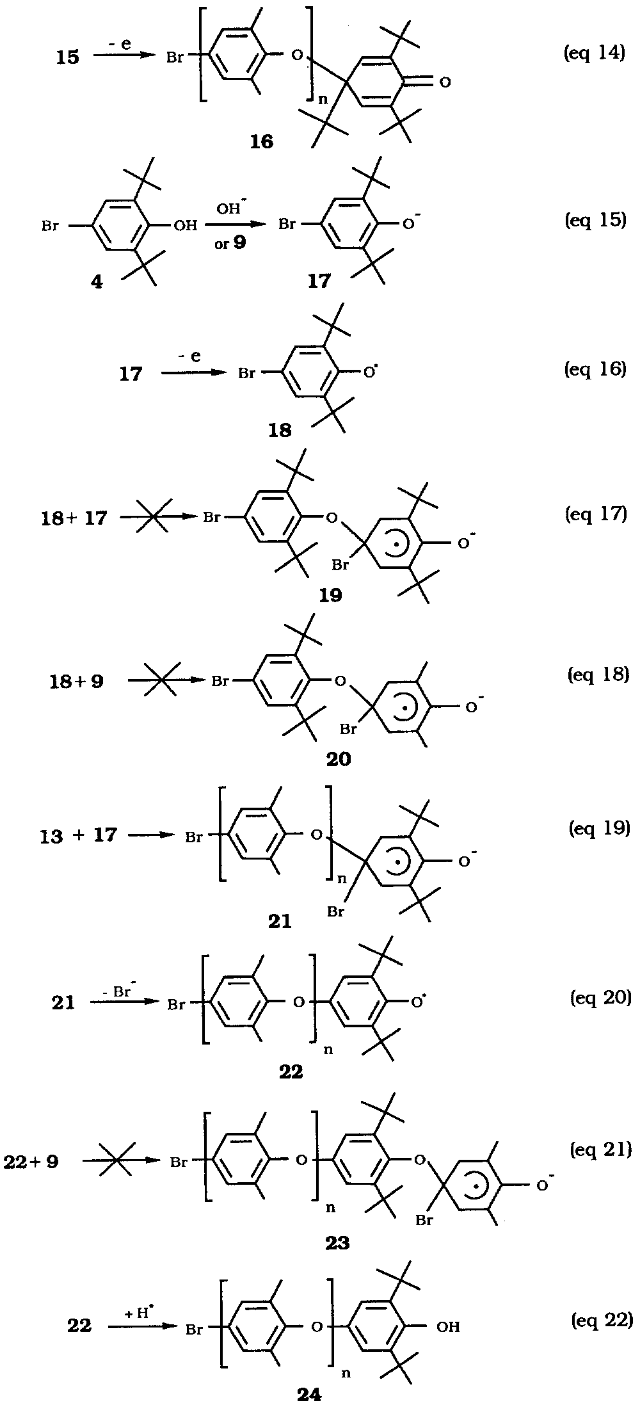


Figure 2. 200 MHz ^{1}H-NMR spectrum ($CDCl_3$, TMS) of the residue after evaporation of benzene from the organic layer (Exp. No. 2, Table I).



Scheme II. The mechanism proposed for the the phase transfer catalyzed polymerization of 4-bromo-2,6-dimethylphenol (**1**) in the presence of 2,4,6-tri-tert-butylphenol (**2**) or 4-bromo-2,6-di-tert-butylphenol (**4**).



Scheme II (Continued)

analysis, the residue consists mostly of unreacted 4-bromo-2,6-dimethylphenol (**1**). Pure 4-bromo-2,6-dimethylphenol was isolated from this residue by recrystallization from petroleum ether. Two resonances due to the tert-butyl groups resulted from the 4-bromo-2,6-di-tert-butylphenol (**4**) are observed. The first resonance at 1.41 ppm indicates the unreacted **4**, the second resonance at 1.36 ppm suggests the presence of 2,6-di-tert-butylphenol group at one chain end of PPO. The aromatic resonance at 6.47 ppm is typical for the aromatic protons of the 2,6-dimethylphenoxy repeating unit of PPO (cf. the assignment structure in Figure 2) oligomer or polymer backbone. The other aromatic resonance at 6.56 ppm was assigned to the 2,6-di-tert-butylphenol end group of a PPO dimer or higher oligomers ($\overline{M}_n$ < 800 g/mol). Figure 2 also demonstrated that only oligomeric PPO was produced as indicated by the ratio of the integrals of G to H.

The second synthetic approach consists of the addition of 4-bromo-2,6-di-tert-butylphenol (**4**) 0.5 and 2.0 h after the homopolymerization of 4-bromo-2,6-dimethylphenol (**1**) was started (eq 3, Scheme I). PPO in 24 to 42% yields were obtained with $\overline{M}_n$ from 1600 to 2400 g/mol from these two experiments (Exp. No. 5 and 6, Table I). The 200 MHz ^{1}H-NMR spectrum of a typical PPO polymer prepared by this method (Exp. No. 6, Table I) is presented in Figure 3. The resonances at 2.09 and 6.47 ppm indicate the repeating unit of PPO polymer backbone. The absence of resonance at 1.41 ppm (Figure 2) suggests that no unreacted 4-bromo-2,6-di-tert-butylphenol was present in the isolated polymer sample. A clear evidence for the 2,6-di-tert-butylphenol chain end is provided by the resonance at 1.36 ppm and 6.56 ppm.

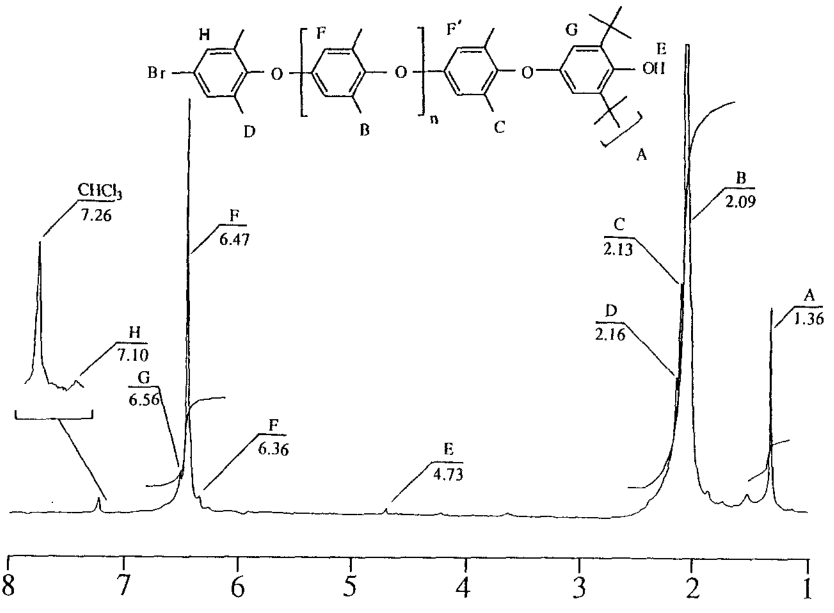


Figure 3. 200 MHz ^{1}H-NMR spectrum (CDCl$_3$, TMS) of the PPO obtained from the polymerization of **1** and **4** (**4** was added 2.0 h after the homopolymerization of **1**).

The mechanism for the polymerization of **1** in the presence of **4** is presented in eq 15-22 from Scheme II. The deprotonation of **4** and the subsequent oxidation of the phenolate **17** are shown in eq 15 and 16 respectively. The attack of 4-bromo-2,6-di-tert-butylphenoxy radical (**18**) on the 4-bromo-2,6-di-tert-butylphenolate (**17**) (eq 17) does not represent a possible reaction due to the steric hindrance of radical **18**. Similar attack of **18** on the 4-bromo-2,6-dimethylphenolate (**9**) (eq 18) is also prohibited by the same steric hindrance. The only possible reaction is shown in eq 19. It consists of an attack of monomeric (n = 1) or oligomeric (n > 1) 2,6-dimethylphenoxy radical **13** on the phenolate **17** at its 4-position yielding the radical-anion **21**. However, for radical-anion **21** the bromide elimination represents a favorable reaction (similar to eq 10) which produces the sterically hindered phenoxy radical **22**. The resulting phenoxy radical **22** is incapable of attacking 4-bromo-2,6-dimethylphenolate (**9**) (eq 21) due to its steric hindrance at the radical site. The phenoxy radical **22** provides an unreactive chain end (i.e, a termination reaction) and forms a 2,6-di-tert-butylphenol terminated dimer or oligomer (eq 22).

Therefore, the copolymerization of **1** in the presence of **4** (experiments 2-4, Table I) produced only some oligomers (Figure 2) when **1** and **4** were added at the beginning of the polymerization, or low yields

PPO of low molecular weights when the addition of **4** was made after the homopolymerization of **1** was started. These results have demonstrated that the 4-bromo-2,6-di-tert-butylphenol (**4**) is a much more powerful chain terminator than 2,4,6-tri-tert-butylphenol (**2**). Two reasons are responsible for the difference between the terminating reactivity of **2** and **4**. First, the steric hindrance in **4** (4-bromo substituent) is much less than that in **2** (4-tert-butyl substituent).[29] Therefore, eq 19 is more favored than eq 13. Secondly, the radical-anion **21** containing the 4-bromo substituent is capable of eliminating its bromide to achieve the benzene ring structure. This leads to a sterically hindered or stable radical **22** which is incapable to propagate. In contrast, the radical-anion **15** containing a 4-tert-butyl group can not eliminate its 4-tert-butyl group and therefore, **15** only dissociates back into the parent radical **13** and anion **6**.

CONCLUSIONS

The phase transfer catalyzed polymerization of 4-bromo-2,6-dimethylphenol (**1**) has been performed in the presence of 2,4,6-tri-tert-butylphenol (**2**) or 4-bromo-2,6-di-tert-butylphenol (**4**). The phenoxy radicals derived from **2** and **4** are sterically hindered by the two bulky tert-butyl groups from the ortho positions of the phenoxy radical site. Therefore, these phenoxy radicals are incapable to propagate. They can only terminate a growing polyphenoxy radical chain derived from the homopolymerization of **1**. The presence of a 4-tert-butyl group creates enough steric hindrance to make **2** a very inefficient chain terminator. In contrast, the reduced steric hindrance in **4** makes the phenoxy radical derived from **4** a more powerful chain terminator which stops the polymerization mostly at dimer and oligomer stage when both **1** and **4** were added at the beginning of the polymerization. Low molecular weight PPO ($\overline{M}_n$ = 1600 - 2400 g/mol) was obtained when **4** was added a short period after the homopolymerization of **1** was started.

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