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Phase transfer catalyzed depolymerization of poly(2,6-dimethyl-1,4-phenylene oxide) in the presence of either 2,4,6-trimethylphenol or 4-tert-butyl-2,6-dimethylphenol

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SUMMARY

This paper describes the phase transfer catalyzed depolymerization of poly(2,6-dimethyl-1,4-phenylene oxide) performed in the presence of either 2,4,6-trimethylphenol or 4-tert-butyl-2,6-dimethylphenol. The structure of the resulting polymers is compared to that of the corresponding polymers obtained by 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. Polymers obtained by depolymerization display a bimodal molecular weight distribution while those obtained by polymerization a monomodal molecular weight distribution. The polymers obtained by direct polymerization present structural units derived from some side reactions. These side reactions do not occur during the depolymerization process.

INTRODUCTION

It seems to be generally accepted that the synthesis of poly(2,6-dimethyl-1,4-phenylene oxide) (PPO) can be performed by using two different reaction mechanisms (1-9). The first one is based on the addition of an aryloxy radical to an aryloxy radical and is considered to be responsible for the oxidative polymerization of 2,6-dimethylphenol (1-8). The second one is based on the addition of an aryloxy radical to a phenolate anion and is responsible for the polymerization of 4-bromo-2,6-dimethylphenol (1-5,7,9).

Recently, we have developed a phase transfer catalyzed procedure for the polymerization of 4-bromo-2,6-dimethylphenol (9,10). 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 leads to poly(2,6-dimethyl-1,4-phenylene oxide)s with one phenol chain end and controllable molecular weight (PPO-OH). This reaction together with its polymerization mechanism were discussed in a previous publication from our laboratory (11).

Both the addition of the aryloxy radical to aryloxy radical and of the aryloxy radical to polymeric phenolate anion are reversible reactions. The radical-radical depolymerization of PPO was investigated (12-15) and it is considered that it stops before the thermodynamic equilibrium is reached (12, 15). However, to our knowledge, there is no report in the literature on the depolymerization of PPO by a radical-anion mechanism. The goal of this paper is to describe the phase transfer catalyzed depolymerization of PPO in the presence of either 2,4,6-trimethylphenol or 4-tert-butyl-2,6-dimethylphenol.

EXPERIMENTAL

Materials

Poly(2,6-dimethyl-1,4-phenylene oxide) (1, PPO, $\overline{\mathrm{Mn}}$=20,000, $\overline{\mathrm{Mw}}/\overline{\mathrm{Mn}}$=3.08) with bimodal molecular weight distribution was obtained from Aldrich. PPO-OH (1, $\overline{\mathrm{Mn}}$=17,800, $\overline{\mathrm{Mw}}/\overline{\mathrm{Mn}}$=1.39) with monomodal molecular weight distribution and the vinyl benzyl ether of 1 (PPO-VBE, $\overline{\mathrm{Mn}}$=26,600, $\overline{\mathrm{Mw}}/\overline{\mathrm{Mn}}$=1.22) were synthesized as reported

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*To whom offprint requests should be sent previously (9,10). 2,4,6-Trimethylphenol (2, 99% from Aldrich), tetrabutylammonium hydrogen sulfate (TBAH, 97% from Aldrich) and the other reagents were used as received or purified by standard methods. 4-tert-Butyl-2,6-dimethylphenol (2') was synthesized as described in a previous publication (11).

Techniques

200 MHz ^{1}H-NMR spectra were recorded on a Varian XL-200 spectrometer. All spectra were obtained from CCl_4 solutions at room temperature, with TMS as internal standard. Molecular weights were determined by gel permeation chromatography (GPC) with a Perkin Elmer series 10 LC instrument equipped with an LC-100 column oven, LC 600 autosampler and a Nelson Analytical 900 Series integrator data station. The measurements were made at 40°C using a UV detector. A set of two Phenomenex-gel columns of $5x10^2$ and 10^4 Å with chloroform as solvent (1.6 ml/min) were used to analyze the polymer obtained from the depolymerization of PPO with bimodal molecular weight distribution. A set of two PL-gel columns of $5x10^2$ and 10^4 Å with chloroform as solvent (1.0 ml/min) were used to analyze the polymer resulted from the depolymerization of the monomodal PPO-OH. The calibration plots of both sets of columns were constructed with polystyrene standards (Supelco). The number average molecular weights of PPO-OH ($\overline{Mn}$=1,000 to 12,000) determined by vapor pressure osmometry agree very well with those determined by GPC calibrated with polystyrene standards. The polystyrene calibrations were therefore used for all subsequent molecular weight calculations.

Phase Transfer Catalyzed Depolymerization of Bimodal PPO (1) in the Presence of Either 2,4,6-Trimethylphenol (2) or 4-tert-Butyl-2,6-dimethylphenol (2')

Depolymerization experiments were performed with different 1/2 and 1/2' molar ratios. An experiment performed with a 1/2 molar ratio of 0.0136/1 is described below. To a solution of 1 (1.00g, 0.05 mmol) in 20 ml benzene was added a solution of 2 (0.50g, 3.67 mmol) in 20 ml of 1.5N aqueous NaOH , followed by 0.1688g (0.5 mmol) of TBAH. The reaction mixture was stirred for 24 hr at room temperature in the presence of air, after which it was quenched by neutralizing with cold 1.5 N HCl. The benzene layer was separated and precipitated in methanol. The precipitate was filtered and dried in vacuo to yield 0.53g (53%) PPO-OH. $\overline{Mn}$=5,700, $\overline{Mw}/\overline{Mn}$=5.79.

Kinetic Experiments of the Phase Transfer Catalyzed Depolymerization of Bimodal PPO (1) in the Presence of either 2,4,6-Trimethylphenol (2) or 4-tert-Butyl-2,6-dimethylphenol (2').

PPO (1, 4.00g, 0.20 mmol) was dissolved in benzene (80 ml). A solution of 2 (0.80g, 5.88 mmol) dissolved in 40 ml of 1.5N NaOH and 0.1031g (0.0304 mmol) TBAH were subsequently added. A sample of 0.5 ml was withdrawn at different reaction times. The sample was neutralized with cold 1.5N HCl. The benzene layer was separated, precipitated in methanol and the precipitate was filtered and dried in vacuo.

Kinetic Experiments of the Phase Transfer Catalyzed Depolymerization of Monomodal PPO-OH (1) in the Presence of 2,4,6-Trimethylphenol (2) or 4-tert-Butyl-2,6-dimethylphenol (2')

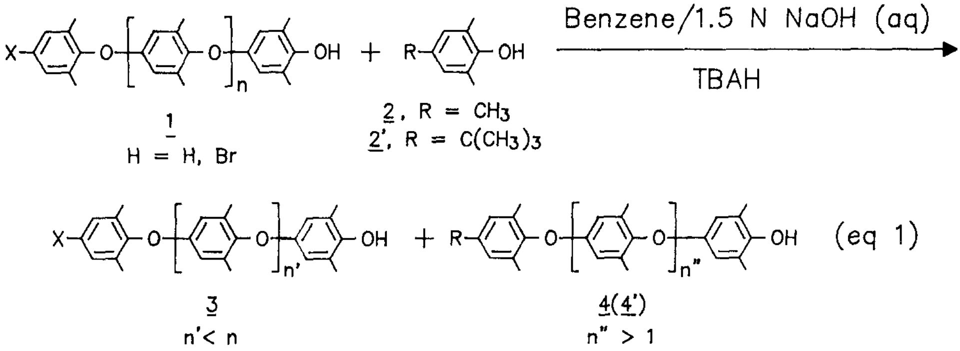
Monomodal PPO-OH (1, 2.00g, 0.112 mmol) was dissolved in a mixture of 12ml benzene and 12ml THF. A solution of 2 (0.20g, 1.5mmol) in 12 ml of 1.5N aqueous NaOH and 0.224g (0.66 mmol) of TBAH were added. The analysis of this depolymerization was performed as described in the previous subsection.

Phase Transfer Catalyzed Depolymerization of the Vinylbenzyl Ether of PPO-OH (PPO-VBE) in the Presence of 4-tert-Butyl-2,6-dimethylphenol (2').

PPO-VBE (0.2371g, 0.0089 mmol) was dissolved in 5 ml benzene. A solution of 2' (0.05g, 0.28 mmol) dissolved in 5 ml 1.5N aqueous NaOH and 0.05g (0.147 mmol) of TBAH were added. The reaction mixture was stirred for 24 hr at room temperature in the presence of air. The reaction was then quenched by neutralizing with cold 1.5 N HCl. The benzene layer was separated and precipitated in methanol to yield 0.2077g (87%) PPO-VBE.

RESULTS AND DISCUSSION

The depolymerization reaction of PPO in the presence of 2 or 2' is represented in Scheme I. Phase transfer catalyzed depolymerization of the bimodal PPO was first performed in the presence of various amounts of 2. The results of these experiments are summarized in Table I. The corresponding GPC traces of the methanol insoluble fractions of the products obtained by depolymerization at different initial 1/2 ratios are plotted in Figure 1. Trace A represents the starting PPO which displays a bimodal molecular weight distribution. Traces B to G correspond to the methanol insoluble polymers obtained by depolymerization at initial 1/2 molar ratios ranging from 0.0068/1 to 0.34/1. They demonstrate that a new GPC peak of lower molecular weight emerged. The area and peak molecular weight of this peak are listed in Table I. They are labelled as "depolymerized PPO-OH". The area of this peak and the peak molecular weight increase with the increase of the initial 1/2 molar ratio (Table I, Figure 1).These results have shown that the molecular weight and the amount of PPO-OH obtained from the depolymerization experiments are both dependent on the initial composition of the depolymerization mixture.



Scheme I. Phase transfer catalyzed depolymerization of PPO-OH (1) in the presence of either 2,4,6-trimethylphenol (2) or 4-tert-butyl-2,6-dimethylphenol (2').

Table I. Synthesis of PPO-OH by Phase Transfer Catalyzed Depolymerization of PPO (1, $\overline{Mn}$ = 20,000; $\overline{Mw}/\overline{Mn}$ = 3.08) in the Presence of Various Amounts of 2,4,6-Trimethylphenol (2); (depolymerization solvents, benzene and 1.5 N aqueous NaOH; depolymerization temperature, 25^{o}C; reaction time, 24 hr; phase transfer catalyst, TBAH).

			Methanol Insoluble PPO-OH from Depolymerization				
Exp. No.	1/2 (wt/wt)	1/2 (mol/mol)	Yield (%)	$\overline{Mn}$ (GPC)	$\overline{Mw}/\overline{Mn}$ (GPC)	Undepolymerized PPO (% area)	Depolymerized PPO (peak $\overline{Mw}$/% area)
1	1/1	0.0068/1	38	20,600	3.32	-	-
2	2/1	0.0136/1	53	5,700	5.79	31	6,700/69
3	5/1	0.034/1	64	4,800	4.82	16	7,000/84
4	10/1	0.068/1	82	5,300	3.47	-	8,100/-
5	16.7/1	0.114/1	86	6,900	3.61	-	11,300/-
6	50/1	0.340/1	87	9,000	3.57	-	14,800/-

The dependence of the polymer composition and molecular weight on the initial 1/2 molar ratio can be interpreted based on the difference of the concentration of 2. The depolymerization process starts from the attack of the 2,4,6-trimethylphenoxy radical on the phenolate chain end of the PPO-OH (16). Since the concentration of 1 is constant throughout these experiments, the concentration of 2,4,6-trimethylphenoxy radical is low at high 1/2 molar ratios. Consequently, fewer chains will be initiated when the 1/2 ratio is high. Therefore, the molecular weight of the polymer resulted from depolymerization will be higher at higher 1/2 molar ratios.At the same time the methanol insoluble fraction separates only the PPO-OH with $\overline{Mn}$ higher than 800. The low molecular weight polymer is soluble in the precipitation mixture and thus will be lost with the methanol soluble fraction. Therefore, the polymer synthesized from low 1/2 ratios will have a higher fraction of lower molecular weight and this low molecular weight fraction will not be separated as part of the methanol insoluble polymer fraction. These effects will contribute to the observed dependences of polymer composition and molecular weight versus the initial 1/2 ratio.

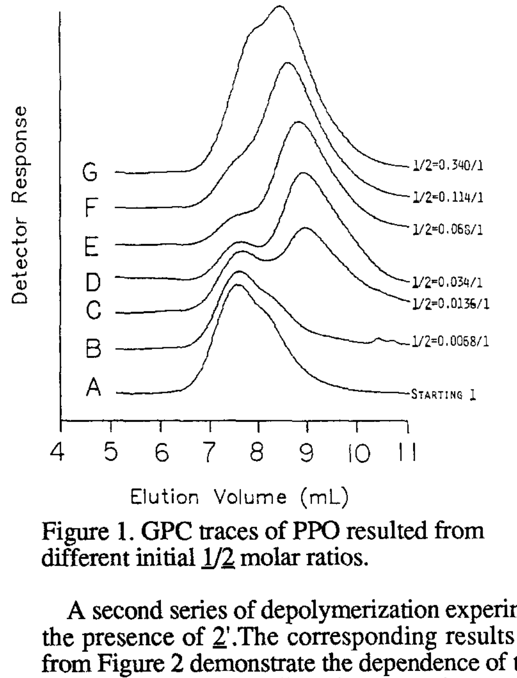


Figure 1. GPC traces of PPO resulted from different initial 1/2 molar ratios.

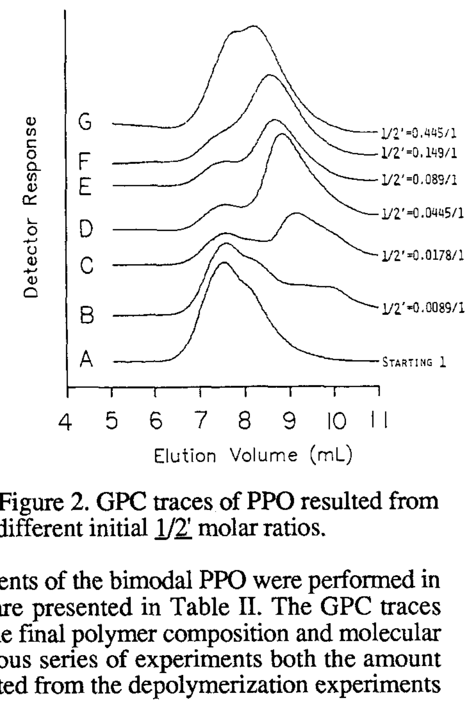


Figure 2. GPC traces of PPO resulted from different initial 1/2' molar ratios.

A second series of depolymerization experiments of the bimodal PPO were performed in the presence of 2'.The corresponding results are presented in Table II. The GPC traces from Figure 2 demonstrate the dependence of the final polymer composition and molecular weight on the initial 1/2' ratio. As in the previous series of experiments both the amount and the molecular weight of the polymers resulted from the depolymerization experiments are increasing with the increase of the 1/2' ratio.

Table II. Synthesis of PPO-OH by Phase Transfer Catalyzed Depolymerization of PPO (1, $\overline{Mn}$ = 20,000; $\overline{Mw}/\overline{Mn}$ = 3.08) in the Presence of Various Amounts of 4-t-Butyl-2,6-Dimethylpenol(2'); (depolymerization solvents, benzene and 1.5 N aqueous NaOH; depolymerization temperature, 25^{o}C; reaction time, 24 hr; phase transfer catalyst, TBAH).

			Methanol Insoluble PPO-OH from Depolymerization				
Exp. No.	1/2' (wt/wt)	1/2' (mol/mol)	Yield (%)	$\overline{Mn}$ (GPC)	$\overline{Mw}/\overline{Mn}$ (GPC)	Undepolymerized PPO (% area)	Depolymerized PPO (peak Mw/% area)
1	1/1	0.0089/1	39	7,000	6.91	-	-
2	2/1	0.0178/1	52	4,400	6.88	33	4,800/67
3	5/1	0.0445/1	73	5,000	4.08	13	7,600/87
4	10/1	0.089/1	86	7,100	4.06	-	9,500/-
5	16.7/1	0.149/1	87	7,600	3.59	-	11,000/-
6	50/1	0.445/1	90	12,500	3.38	-	20,000/-

The 200 MHz ^{1}H-NMR spectra of the methanol insoluble PPO-OH obtained from the depolymerization of 1 in the presence of 2 are shown in Figure 3. The resonance due to the 2,4,6-trimethylphenoxy chain end is present in all samples at 6.80 ppm. However, with the exception of spectrum B, none of these spectra exhibit the benzyl ether resonance from 4.59 ppm. This resonance appears in all PPO-OH obtained by the phase transfer catalyzed polymerization of 4-bromo-2,6-dimethylphenol in the presence of 2 and corresponds to the benzyl ether structural units derived from a side reaction of 2 (11). The NMR spectra of the PPO-OH resulted from the depolymerization of 1 in the presence of 2' are presented in Figure 4. All these spectra present the resonance at 6.98 ppm which is due to the 4-tert-butyl-2,6-dimethylphenoxy chain end.

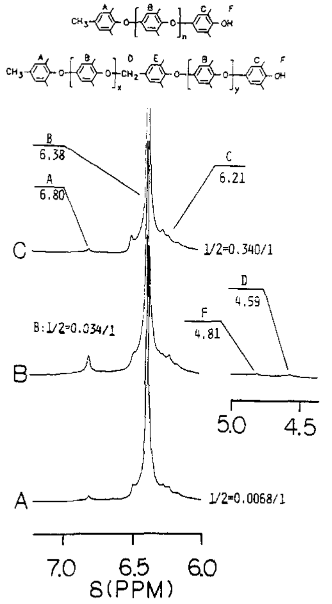


Figure 3. 200 MHz ^{1} H-NMR spectra of PPO resulted from different initial 1/2 molar ratios.

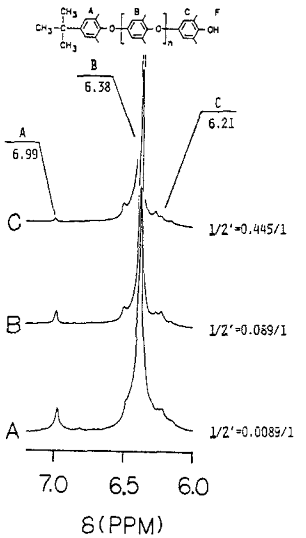


Figure 4. 200 MHz ^{1}H-NMR spectra of PPO resulted from different initial 1/2' molar ratios.

The depolymerization of the bimodal 1 in the presence of 2 was investigated as a function of the reaction time for a 1/2 molar ratio of 0.034/1.The GPC traces of the methanol insoluble PPO-OH fractions resulted from this reaction are presented in Figure 5. Both the amount and the molecular weight of the newly formed PPO-OH increase with the increase of reaction time. The rate of formation of the new PPO-OH fraction decreases with the reaction time and reaches a plateau at 64% methanol insoluble PPO. The amount of PPO obtained by depolymerization is plotted as a function of the reaction time in Figure 6.

A sample of monomodal PPO-OH with $\overline{Mn}$=17,800 and $\overline{Mw}/\overline{Mn}$=1.39 was depolymerized in the presence of 2 at an initial ratio 1/2=0.068/1. The GPC traces of the methanol insoluble PPO-OH obtained at several different reaction times are presented in Figure 7. After 24 hr of depolymerization time the newly formed PPO-OH represents 91.6% of the entire polymer sample (trace D in Figure 7). The amount of PPO-OH formed during this depolymerization is plotted as a function of the reaction time in Figure 8. The depolymerization of PPO-OH with monomodal molecular weight distribution was performed also in the presence of 2'. The GPC traces of the polymer resulted at different reaction times are shown in Figure 9. The amount of PPO-OH formed by depolymerization of a 1/2' ratio of 0.089/1 is plotted in Figure 10 as a function of the reaction time. This plot demonstrates that the rate of depolymerization of 1 in the presence of 2' is higher than that in the presence of 2. This difference may be attributed to the higher lipophilicity of 2' versus that of 2.

The depolymerization of PPO-VBE in the presence of 2 leads to a polymer with identical molecular weight and NMR spectrum as that of the starting polymer.Therefore, the protection of the PPO-OH with an ether group avoids the depolymerization reaction. This experiment demonstrates that depolymerization of PPO-OH is initiated by the attack of a phenoxy radical on the terminal phenolate unit of the PPO-OH.

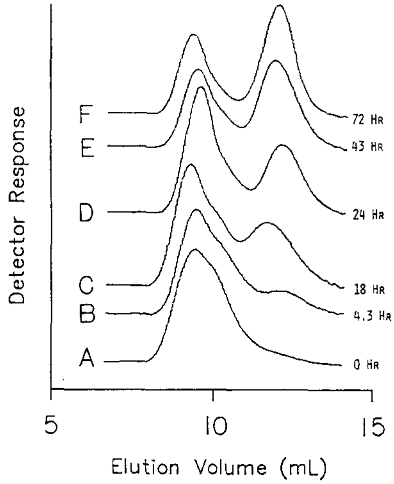


Figure 5. GPC traces of PPO resulted from bimodal 1 at different reaction times (1/2=0.034/1).

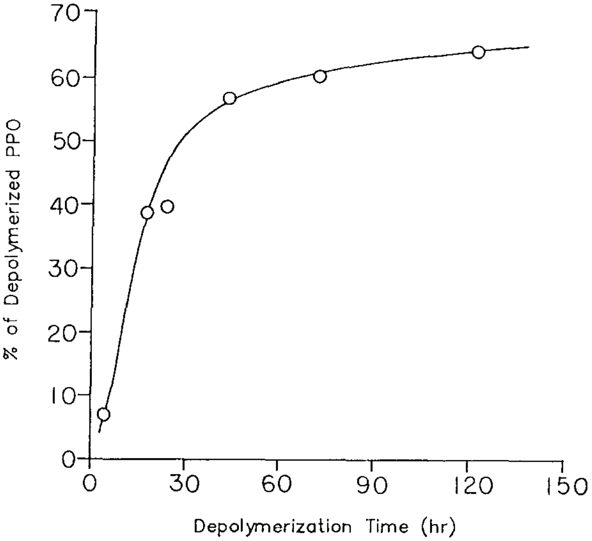


Figure 6. Dependence of % depolymerized 1 on reaction time (1/2=0.034/1).

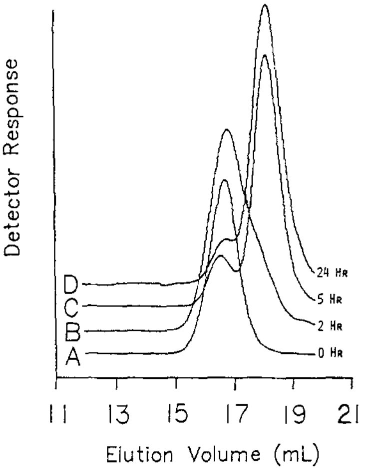


Figure 7. GPC traces of PPO-OH resulted from monomodal 1 in the presence of 2 at different reaction times (1/2=0.068/1).

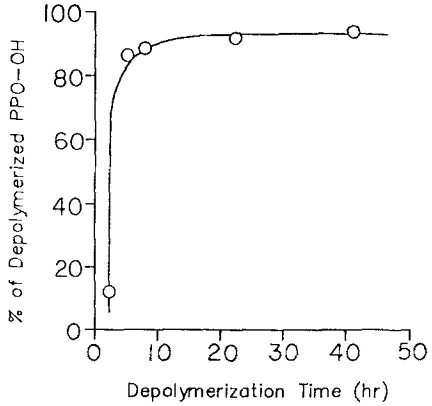


Figure 8. Dependence of % depolymerized 1 on reaction time (monomodal 1 in the presence of 2.

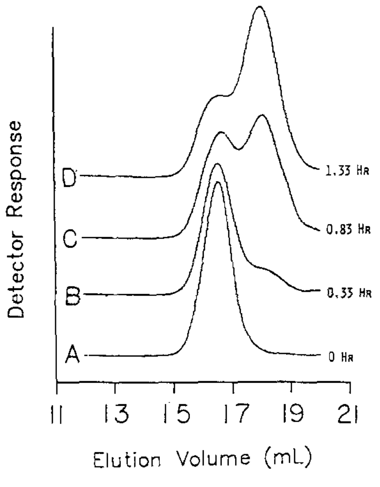


Figure 9. GPC traces of PPO-OH resulted from monomodal 1 in the presence of 2' at different reaction times (1/2'=0.089/1).

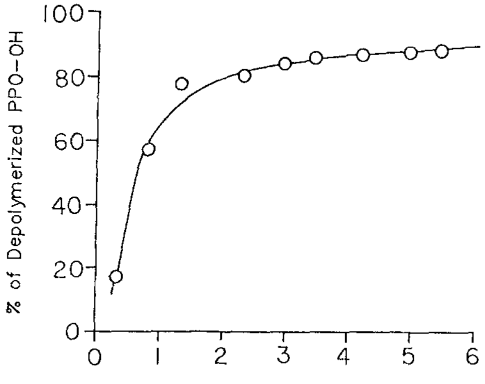


Figure 10. Dependence of % depolymerized 1 on the reaction time (monomodal 1 in the presence of 2'.

The depolymerization experiments described in this paper have demonstrated that PPO-OH with various molecular weights can be synthesized either by the phase transfer catalyzed polymerization of 4-bromo-2,6-dimethylphenol in the presence of 2,4,6-

trimethylphenol or 4-tert-butyl-2,6-dimethylphenol, or by the phase transfer catalyzed depolymerization of PPO-OH in the presence of the same two phenols. While the polymers synthesized by polymerization display a monomodal molecular weight distribution (11), the polymers obtained by depolymerization display a bimodal molecular weight distribution. The PPO-OH synthesized by the polymerization of 4-bromo-2,6-dimethylphenol in the presence of 2,4,6-trimethylphenol contains benzylic structural units derived from some side reactions of 2,4,6-trimethylphenol. The PPO-OH obtained by the corresponding depolymerization reaction does not contain these benzylic structural units. The accompanying publication will describe an anion-radical mechanism which supports these depolymerization results and accounts for the absence of side reactions in these depolymerization experiments.

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