

A radical-anion mechanism for the phase transfer catalyzed depolymerization of poly(2,6-dimethyl-1,4-phenylene oxide)

V. Percec* and J. H. Wang

Department of Macromolecular Science, Case Western Reserve University, Cleveland, OH 44106, USA

SUMMARY

This paper describes a novel mechanism for the depolymerization of poly(2,6-dimethyl-1,4-phenylene oxide). This radical-anion mechanism is responsible for liquid (organic solvent)-liquid (aqueous inorganic base) phase transfer catalyzed depolymerization of poly(2,6-dimethyl-1,4-phenylene oxide). This depolymerization occurs through the addition of an aryloxy radical to the terminal phenolate anion of the polymer. The particular example discussed in this paper refers to the 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. The similarities and differences between the phase transfer catalyzed polymerization of 4-bromo-2,6-dimethylphenol in the presence of 2,4,6-trimethylphenol and 4-tert-butyl-2,6-dimethylphenol and the phase transfer catalyzed depolymerization of poly(2,6-dimethyl-1,4-phenylene oxide) in the presence of the same two phenols are discussed.

INTRODUCTION

In some previous publications from our laboratory we have presented a novel preparative method for the synthesis of poly(2,6-dimethyl-1,4-phenylene oxide). This method consists of the phase transfer catalyzed polymerization of 4-bromo-2,6-dimethylphenol in the presence of air (1-3). When this reaction is performed in the presence of 2,4,6-trimethylphenol or 4-tert-butyl-2,6-dimethylphenol, polymers with well defined molecular weight and chain end functionalities are obtained (3). The mechanism of this polymerization reaction is based on the addition of an aryloxy radical to an arylphenolate anion and was discussed in detail (1, 3). Although the propagation step of this reaction, i.e., the addition of the aryloxy radical to the 4-bromo-2,6-dimethylphenolate anion is not reversible, the addition of the aryloxy radical to the terminal phenolate anion is reversible. Therefore, in the absence of 4-bromo-2,6-dimethylphenolate anions, a depolymerization reaction should occur. This depolymerization process should follow a similar radical-anion mechanism as the polymerization process.

The depolymerization of poly(2,6-dimethyl-1,4-phenylene oxide) by a radical-radical mechanism i.e., addition of an aryloxy radical to an aryloxy radical was repeatedly investigated (4-11). However, the first experiments on the depolymerization of poly(2,6-dimethyl-1,4-phenylene oxide) which is considered to take place by a radical-anion mechanism were reported for the first time in the accompanying publication (12).

The goal of this paper is to present a radical-anion mechanism which can account for the results obtained during the phase transfer catalyzed depolymerization of poly(2,6-dimethyl-1,4-phenylene oxide) in the presence of 2,4,6-trimethylphenol and 4-tert-butyl-2,6-dimethylphenol (12).

*To whom offprint requests should be sent

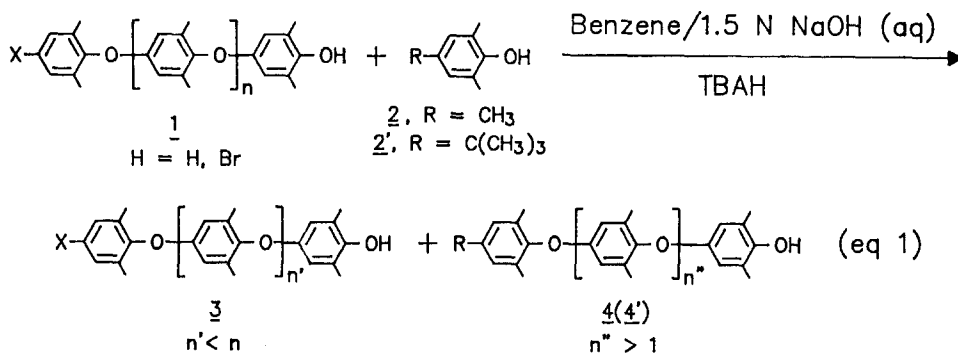
EXPERIMENTAL

The liquid (organic solvent)-liquid (aqueous inorganic base) 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 was described in the previous publication (12).

RESULTS AND DISCUSSION

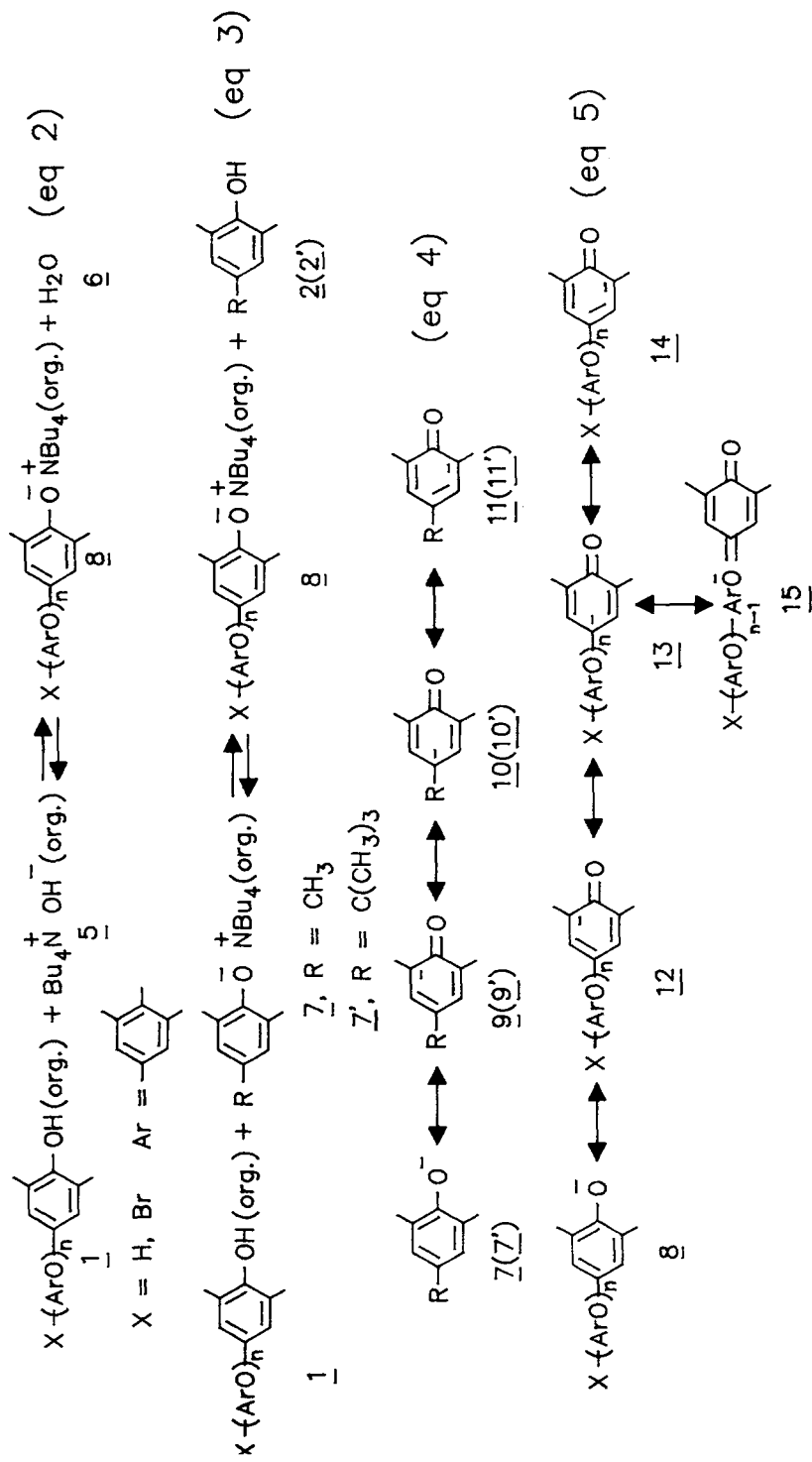
The mechanisms of the phase transfer catalyzed homopolymerization of 4-bromo-2,6-dimethylphenol and of the phase transfer catalyzed polymerization of 4-bromo-2,6-dimethylphenol in the presence of 2,4,6-trimethylphenol and 4-tert-butyl-2,6-dimethylphenol were discussed previously (1, 3).

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



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').

The deprotonation mechanism of the PPO-OH is presented in Scheme II. PPO-OH is insoluble in the aqueous NaOH solution. Thus its phenol chain end can be deprotonated only in the organic (benzene) phase and at the interface between the organic and aqueous NaOH phases. The deprotonation at the interface is a slow process. In the phase transfer catalyzed reaction, the first possible deprotonation reaction is presented in equation 2 from Scheme II. This is the deprotonation of PPO-OH 1 by the OH⁻ which is transferred into the organic phase in the form of the tetrabutylammonium hydroxide 5. This process is however slow due to the low lipophilicity of the tetrabutylammonium hydroxide 5 (13, 14). The second possible deprotonation reaction is presented in equation 3 from Scheme II. It consists of the deprotonation of PPO-OH 1, by the tetrabutylammonium phenolate 7. Due to the high lipophilicity of this organic onium phenolate, equation 3 is kinetically more favored than equation 2. The resonance structures of the monomeric phenolate 7 are shown as structures 7, 9, 10, and 11 (equation 4, Scheme II). The corresponding five resonance structures of the polymeric phenolate 8 i.e., 8, 12, 13, 14, and 15 are shown in equation 5 from Scheme II. In the resonance structure 15 the charge of the anion is delocalized on the aryloxy oxygen. This resonance structure is stable due to the high electronegativity of oxygen (15). In contrast, 7 has an electron-donating group which increases the electron density of the phenylene ring. This combination of effects makes the monomeric phenolate 7 a stronger Lewis base than the polymeric phenolate 8. Consequently, 1 which is the conjugate acid of 8 represents a stronger Lewis acid than 2 (Scheme I). Therefore, since the deprotonation reaction represents an acid-base equilibrium between a strong Lewis acid 1 and a strong Lewis base 7, its equilibrium is shifted towards the right side (equation 3,



Scheme II. The deprotonation mechanism of PPO-OH (1) during the phase transfer catalyzed depolymerization reactions.

Scheme II). Thus, equation 3 from Scheme II represents the thermodynamically favored deprotonation reaction.

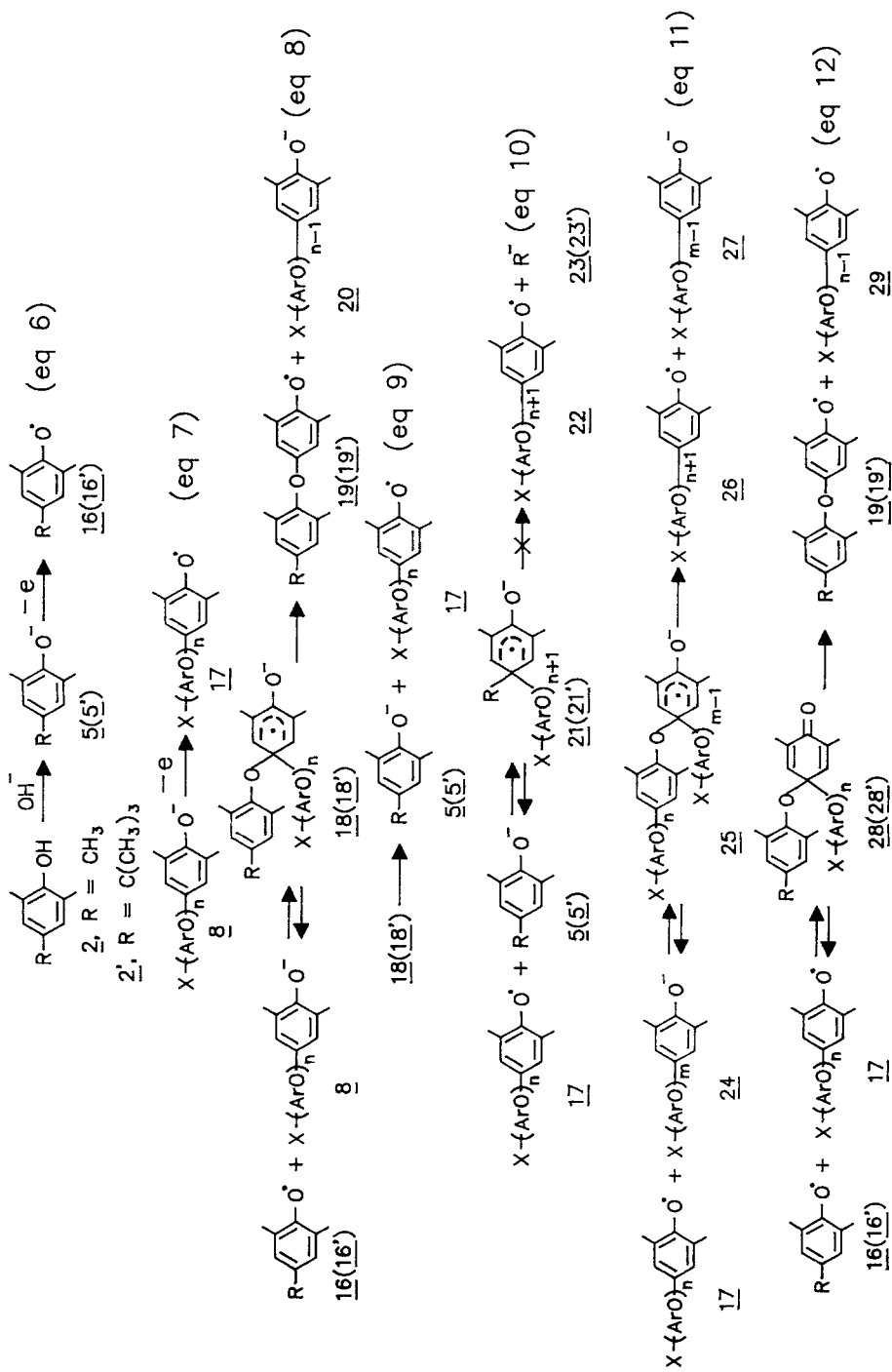
The depolymerization mechanism of the phase transfer catalyzed process is presented in Scheme III. Equation 6 shows the generation of the phenoxy radical 16 through the oxidation of the corresponding phenolate 5 by air-oxygen. This process was discussed in detail previously (1, 3). The oxidation of polymer phenolate 8 is outlined in equation 7. Due to the low concentration of polymeric phenolate 8, equation 7 is not favored kinetically. In the previous paper we have demonstrated that a PPO-OH whose phenol end group is protected with an ether group does not undergo depolymerization (12). Therefore, the depolymerization reaction starts from the attack of phenoxy radical 16 on the para position of the terminal phenolate unit of 8 (equation 8, Scheme III). The attack of the phenoxy radical 16 on the internal PPO units is not allowed. The resulting radical anion 18 has three possibilities to break the ether bond. The first one is the reversible reaction leading to 16 and 8. The second path leads to the dimeric radical 19 and the phenolate 20 which has a lower degree of polymerization. The third breaking pathway is shown in equation 9, and leads to the phenolate 5 and the radical 17. However, equation 9 is not favored thermodynamically since no new bond is formed. An additional contribution to the low probability of equation 9 is provided by the fact that the lipophilicity of 5 is lower than that of 8 and 20.

The attack of the low concentration of polymer radical 17, if generated at all by equation 7, on the monomer phenolate 5 (equation 10) leads to the intermediate 21 which can not generate 22 and 23 due to the strong R-C bond. The reaction of the polymeric radical 17 with the polymeric anion 24 is outlined in equation 11. Equation 12 represents an equilibrium reaction. The redistribution between the radicals 16 and 17 from equation 12 provides an alternative mechanism for the depolymerization reaction. The quinone ketal intermediate 28 decomposes either to the starting radicals 16 and 17 or to a pair of redistributed radicals 19 and 29. Considering the low concentration of the radicals available under the reaction conditions of the phase transfer catalyzed process, equation 12 represents the least probable reaction.

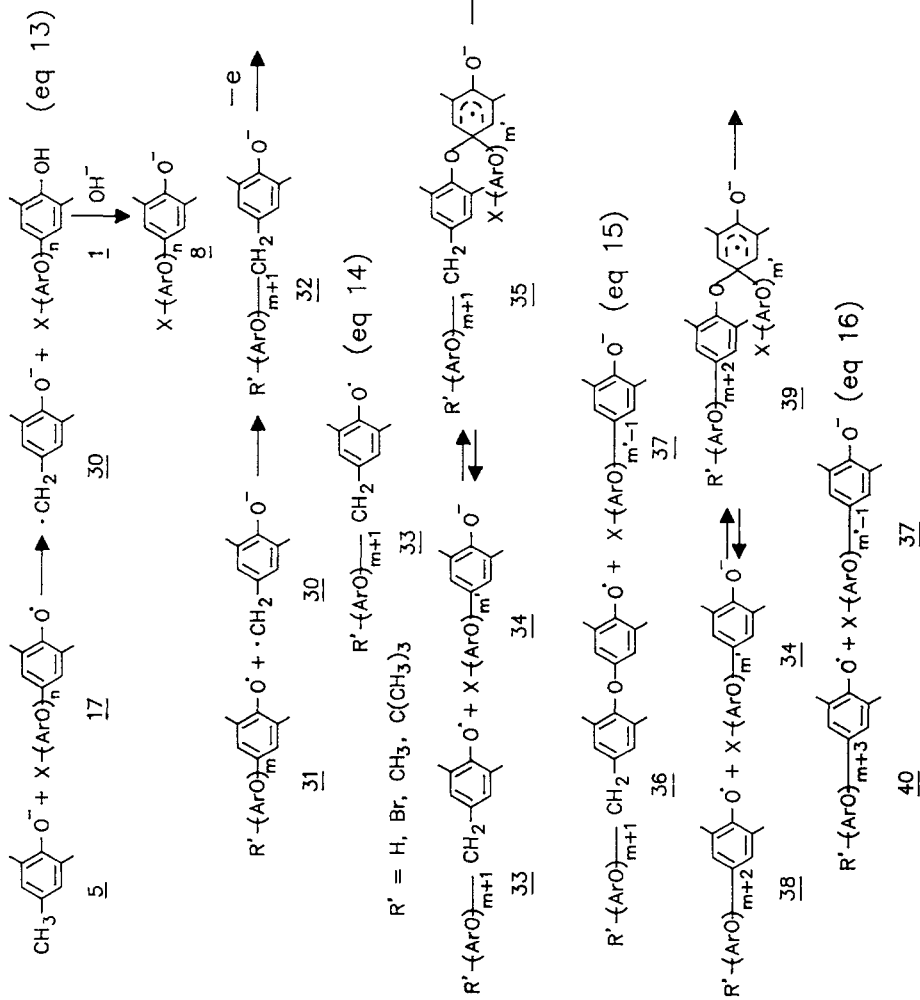
In conclusion, the redistribution reaction of the phase transfer catalyzed depolymerization proceeds according to a radical anion mechanism as shown in equation 8 from Scheme III.

The depolymerization through equation 8 (Scheme III) results in PPO-OH with either 2,4,6-trimethylphenoxy or 4-tert-butyl-2,6-dimethylphenoxy chain ends. This reaction generates two polymer distributions. Both the molecular weights and the amounts of these two polymer distributions are determined by the initial $1/2$ and $1/2'$ molar ratios since they dictate the initial concentration of the radical 16 (12).

During the phase transfer catalyzed polymerization of 4-bromo-2,6-dimethylphenol in the presence of 2,4,6-trimethylphenol (2), 2 participates in a side reaction as that described in equation 13 from Scheme IV. This side reaction consists of the α -hydrogen abstraction from the phenolate 5 by a polymeric radical 17 and leads to the radical anion 30. The intermediate 30, if generated at all, will participate in the polymerization reaction (equation 14, Scheme IV) leading to a polymeric radical containing benzyl ether units. As shown in the previous paper (12), the NMR spectra of most PPO-OH obtained from the depolymerization of PPO-OH in the presence of 2 do not contain such structural units. Only the polymer obtained from $1/2$ molar ratio of 0.034/1 contains a very small concentration of such structural units. There are several parameters which can explain the generation of a low concentration of benzyl ether structural units during the depolymerization process (eq. 13, 14, and 15 in Scheme IV). First, during the depolymerization process the concentration of the polymeric radical 17 is very low due to the unfavored reactions represented by equations 7 and 9 from Scheme III. Therefore, this determines that the concentration of radical anion 30 generated in equation 13 is very low. Second, the low concentrations of 31 and 30 make the equation 14 less favored kinetically. Third, the reactivity of 33 containing a benzyl ether unit is lower than that of 38 due to the stabilization by hyperconjugation through the α -hydrogens of 33 (3). Therefore, equation 15 is less favored than equation 16. This makes the participation of 33 in the



Scheme III. Radical-anion mechanism of the phase transfer catalyzed depolymerization.



Scheme IV. Possible side reactions of 2,4,6-trimethylphenol.

depolymerization reaction to be kinetically unfavored. For all these reasons, the side reactions from equations 13, 14 and 15 are less probable during the phase transfer catalyzed depolymerization than during the phase transfer catalyzed polymerization process. Therefore, the PPO-OH obtained from the depolymerization of PPO-OH in the presence of 2 does not contain at all or contains only a very low concentration of benzyl ether structural units derived from 2.

ACKNOWLEDGMENT

Acknowledgment is made to the donors of the Petroleum Research Fund administered by the American Chemical Society and NATO (traveling grant) for the support of this research.

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Accepted April 14, 1990

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