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Synthesis of aromatic polyethers by ion-radical reactions

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SYNTHESIS OF AROMATIC POLYETHERS
BY ION-RADICAL REACTIONS

by

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Submitted in partial fulfillment of the requirements
for the Degree of Doctor of Philosophy

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May, 1991
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GRADUATE STUDIES

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SYNTHESIS OF AROMATIC POLYETHERS
BY ION-RADICAL REACTIONS

ABSTRACT
by
JAMES HONGXUE WANG

This dissertation describes the synthesis of aromatic polyethers by both anion-radical and cation-radical reactions. The anion-radical reactions refer to the phase transfer catalyzed (PTC) copolymerization of 4-bromo-2,6-dimethylphenol (BDMP) with a comonomer phenol and the PTC depolymerization of poly(2,6-dimethyl-1,4-phenylene oxides) (PPO) in the presence of a phenol.

The PTC anion-radical copolymerization of BDMP with a chain initiator - 2,4,6-trimethylphenol (TMP) or 4-tert-butyl-2,6-dimethylphenol (TBDMP) led to PPO with one ω-(2,6-dimethylphenol) chain end (PPO-OH). The molecular weight of the PPO-OH is controlled by the molar ratios of BDMP/TMP or BDMP/TBDMP. The PTC copolymerization of BDMP with 2,2-bis(4-hydroxy-3,5-dimethylphenyl)propane yielded α,ω-bis(2,6-dimethylphenol)-PPO (PPO-2OH).

The PTC copolymerization of BDMP with 4-hydroxy-3,5-dimethylbenzyl alcohol resulted in a mixture of PPO-2OH and PPO-OH. Chain termination was observed in the PTC copolymerization of BDMP with a 4-substituted-2,6-di-tert-butylphenol. The PTC anion-radical depolymerization of high molecular weight PPO-OH in the presence of either TMP or TBDMP was investigated. Anion-radical polymerization and depolymerization mechanisms were proposed for these PTC reactions.

The cation-radical polymerization of a series of bis(aromatic groups) substituted ether monomers was investigated. A series of monomers of different
structure were synthesized and polymerized under single electron transfer (SET) oxidation conditions (the Scholl reaction). The low polymerizability of 4,4'-bis(phenoxy)diphenyl sulfones and 4,4'-bis(phenylthio)diphenyl sulfone monomers is determined by the low oxidizability/nucleophilicity of the phenoxy/phenylthio polymerizable groups. The substitution of the phenyl rings with electron-donating groups improves both the polymerizability and the solubility of the polymers. The polymerizability of 4,4'-bis(1-naphthoxy)diphenyl sulfone is higher than that of 1,5-bis(1-naphthoxy)pentane. The difference between the reactivity of growing cation-radical species is a dominant factor since this difference is suggested to be larger than the difference between the nucleophilicity of the monomers. The cation-radical copolymerization of α,ω-bis[4-(1-naphthoxy)phenylsulfonyl]perfluoroalkanes and 1,5-bis(1-naphthoxy)diphenyl sulfone indicates that the comonomer of higher oxidizability/nucleophilicity is more favorably incorporated into the copolymers. Fully aromatic polyethers were synthesized by the cation-radical polymerization of bis(1-naphthoxy)aryls. The factors determining the polymerizability of a monomer and the monomer structure/polymerizability relationship for the cation-radical polymerization are suggested.

The "reactivity" of the ω-(p-vinylbenzyl) ether macromonomer of PPO (PPO-VBE, M2) in copolymerization with methyl methacrylate (M1) was investigated as a function of macromonomer concentration and the nature of polymerization solvents. The reactivity of the PPO-VBE macromonomer, 1/r1, was influenced by both the concentration of the macromonomers and by the nature of polymerization solvents. Micelle formation of the resulting graft copolymers was demonstrated by 1H-NMR spectroscopy. The concentration and solvent effects
were interpreted based on the micelle formation during the copolymerization, which causes the partition of comonomer concentrations between the bulk of free solvent and around the growing chains.
DEDICATION

This dissertation is dedicated to my wife, Lisha, to my parents, Xiuyi Wang, Shuzen Wang, and Shumei Wang, and to my parents-in-law, Qingnian Yu and Honglan Zhou, for their love, support, and encouragements.
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CHAPTER 1

GENERAL INTRODUCTION

1.1. MECHANISMS OF AROMATIC NUCLEOPHILIC SUBSTITUTIONS

Aromatic electrophiles undergo nucleophilic substitutions (eq 1) by four mechanisms: S_N1, S_NAr, Aryne, and S_{RN}1.\textsuperscript{1-3} Aromatic nucleophilic substitutions are also accomplished by metal catalyzed reactions.\textsuperscript{2-3} The leaving group is usually a halogen or a nitro group. The nucleophiles include most of the nucleophilic groups derived from IVA, VA, and VIA elements such as phenoxides, alkoxides, sulfide, fluoride, amines, and carbanions. The reaction mechanism is determined by the nature of the aromatic electrophile, the leaving group, the nucleophile, and the reaction conditions. The aromatic nucleophilic substitution reactions are used to synthesize many classes of high performance aromatic polyethers (Section 1.3).

\[
\text{ArX} + \text{Nu}^- \longrightarrow \text{ArNu} + \text{X}^- \quad (1)
\]

\[\text{ArX} = \text{Aromatic Electrophile}; \text{X} = \text{Leaving Group}; \text{Nu}^- = \text{Nucleophile.}\]

1.1.1 The S_N1 Mechanism

The S_N1 mechanism is a unimolecular nucleophilic substitution. The first step is the dissociation of the aromatic electrophile into an aryl cation. The nucleophilic attack occurs in the second step. So far the only aromatic electrophiles that react by this mechanism are the diazonium salts.\textsuperscript{2,4} The unimolecular decomposition of a diazonium salt leads to an aryl cation and nitrogen (eq 2). The
resulting aryl cation is highly reactive and therefore undergoes nucleophilic reactions with either a nucleophile or with a solvent molecule. The \( S_N1 \) mechanism is responsible for the hydrolysis of diazonium salts to phenols.\(^4\,^5\)

\[
\text{ArN}_2^+ \rightarrow \text{Ar}^+ + \text{N}_2 \quad (2)
\]

\[
\text{Ar}^+ + \text{Nu}^- \rightarrow \text{ArNu} \quad (3)
\]

The \( S_N1 \) mechanism is supported by numerous experimental observations. First of all, the reaction is first order in diazonium salt and independent of the nucleophile concentration.\(^4\) Secondly, substituent effects are consistent with a unimolecular rate determining step.\(^6\) Thirdly, the reaction has a prominent isotope effect for ortho deuterium substitution (1.22).\(^7\) Finally, the change in the positions of isotopically labelled-N in the diazonium salts can only be rationalized based on the initial release of nitrogen and its subsequent return to the phenyl cation.\(^8\)

However, it should be noted that aryl diazonium salts also react by two non-\( S_N1 \) mechanisms under other conditions. One mechanism is proposed for the reaction of diazonium salt with azide ion.\(^7\) The mechanism consists of the addition of the nucleophile to the diazonium salt and its subsequent release of nitrogen. The other non-\( S_N1 \) mechanism is suggested for the Sandmeyer reaction which involves a single electron transfer (SET) between the aryl diazonium salt and the copper(I) catalyst and the subsequent halide transfer from copper.\(^3\)

1.1.2. The \( S_NAr \) Mechanism

In contrast to the \( S_N1 \) mechanism, the \( S_NAr \) (i.e. aromatic nucleophilic substitution) mechanism is a bimolecular process which occurs in two steps. This
mechanism has also been termed as the $S_N2Ar$, the addition-elimination, and the intermediate complex mechanism. The first step in the $S_NAr$ mechanism is a nucleophilic addition of nucleophile to the aromatic electrophile leading to a Meisenheimer complex (eq 4). This reaction step is slow and is therefore rate-determining. The subsequent elimination of the leaving group yields the substitution product (eq 5). Only activated aromatic compounds, i.e. the aromatic substituted at ortho or para positions with one or more strong electron-withdrawing substituents such as sulfonyl, carbonyl, nitro, cyano, trifluoromethyl, etc., undergo nucleophilic substitutions by this mechanism. The presence of the activating substituents on the aromatic ring stabilizes the Meisenheimer complex and therefore enhances the rate constant of the the rate-determining step.

\[
\begin{align*}
S & \quad \overset{X}{\text{aryl}} + Nu^- \quad \text{slow} \quad \rightarrow \quad S \quad \overset{X}{\text{aryl}} \quad Nu \\
& \quad \text{Meisenheimer} \\
& \quad \text{Complex} \\
\end{align*}
\]

\[
\begin{align*}
S & \quad \overset{X}{\text{aryl}} \quad Nu \quad \text{fast} \quad \rightarrow \quad S \quad \overset{Nu}{\text{aryl}} \quad Nu + X^- \\
S & = -\text{NO}_2, -\text{SO}_2^-, -\text{CN}, -\text{CO}_2, -\text{CF}_3, \text{etc.}
\end{align*}
\]

The isolation of the Meisenheimer salt from the reaction of ethyl picrate and methoxide ion provided a convincing evidence for the mechanism.\(^9\) The order of the relative reactivity of different halogens follows $F >> Cl > Br > I$.\(^{10}\) This order supports the mechanism in which C-X bond is broken after the rate-determining step. The fact that fluoro group is the best leaving group results from the reduction of electron density at the substituted carbon due to the high electronegativity of the
fluoro group (the Pauling electronegativity for F : Cl : Br : I is 4.0 : 3.0 : 2.8 : 2.5\textsuperscript{11}). Therefore the fluoro group enhances the rate constant of the generation of the Meisenheimer complex more than other halogens. Additional evidence for the two step mechanism comes from the base catalysis for the aromatic electrophiles with poor leaving groups (e.g. OR group) in reactions with relatively bulky amine nucleophiles.\textsuperscript{12,13}

Recently, it has been demonstrated that the formation of Meisenheimer complex involves additional steps,\textsuperscript{14-19} which occurs through a single electron transfer mechanism. The aromatic electrophile is reduced to its anion-radical by a single electron transfer and subsequently couples with the radical derived from the nucleophile (eq 6).

\[
\begin{align*}
\text{Ar-}X + \text{Nu}^- & \quad \overset{\pi-\text{Complex}}{\xrightarrow{\text{Charge Transfer Complex}}} \quad \text{Ar}^- \cdot \cdot \cdot \text{Nu}^- \\
 & \quad \overset{\text{Meisenheimer Complex}}{\xrightarrow{\text{Nu}}} \quad \text{Ar}^- \left< \begin{array}{c}
X \\
\text{Nu}
\end{array} \right>
\end{align*}
\]

(6)

1.1.3. The Aryne Mechanism

This mechanism is responsible for the substitution reaction of non-activated aryl halide under strongly basic conditions such as amide anion in liquid ammonia. Roberts and his co-workers first proposed the benzyne intermediate based on their results on the transformation of chlorobenzene into aniline by reacting with potassium amide in liquid ammonia.\textsuperscript{20} Other aromatic nucleophilic substitutions only yield one product. However, the reaction of substituted or isotopically labelled aryl halide proceeds by this mechanism leading to two substitution products in about identical yields. In the first step the elimination of a proton and the leaving
group yields a highly reactive intermediate aryne (eq 7). The nucleophile subsequently attacks both positions of the "triple bond" with about equal probability leading to two substitution products (eq 8).

The fact that the aryl halides substituted at both ortho positions do not react under the aryne conditions supports the mechanism. The order of relative reactivity of halogens is Br > I > Cl >> F. This order is interpreted by the balanced effects of the ease of proton removal (F > Cl > Br > I) and the ease of C-X bond cleavage (I > Br > Cl > F). Therefore, for Br and I, the proton removal is the rate-determining step. However for Cl and F, the C-X bond cleavage is the rate-determining. Besides the strong basic conditions, arynes can also be formed by other methods, such as the thermal decomposition of the diazotized o-aminobenzoic acids22 or 1-aminobenzotriazole.23

\[ \text{ Aryne } \]

\[ \begin{align*}
\text{S} & \quad X \quad \text{H} + B^- \rightarrow \text{S} \quad \text{H} + BH + X^- \\
\text{B}^- & = \text{base}
\end{align*} \]  

(7)

\[ \begin{align*}
\text{S} & \quad \text{H} + \text{Nu}^- + H^+ \rightarrow \text{S} \quad \text{Nu} \quad \text{H} + \text{S} \quad \text{Nu} \\
\text{S} & \quad \text{H} \quad \text{Nu}
\end{align*} \]  

(8)

1.1.4. The $\text{S}_{\text{RN1}}$ Mechanism

In 1970, Kim and Bunnett first proposed the $\text{S}_{\text{RN1}}$ mechanism of aromatic nucleophilic substitution.24 In contrast to all the other mechanisms, the $\text{S}_{\text{RN1}}$ mechanism is a chain reaction which consists of four steps.25-27 A chain is initiated by a single electron reduction of the aromatic electrophile to form its corresponding anion-radical (eq 9). The initiation is effected either by reactions with solvated
electrons (i.e. alkali metal dissolved in liquid ammonia), by reduction at a cathode, by electron transfer from another anion-radical, or by photostimulation.\textsuperscript{25-27} In the chain propagation steps (eqs 10-12), the anion-radical first dissociates into an aryl radical and the anion of the leaving group (eq 10). The aryl radical subsequently participates in nucleophilic reaction with a nucleophile to form a nucleophile \(\sigma\)-bonded anion-radical (eq 11). The single electron transfer of the aryl-nucleophile anion-radical with a neutral aromatic electrophile leads to the substitution product (ArNu) and regenerates an electrophile anion-radical (eq 12). The chain propagation proceeds by the reaction sequences in eqs 10-12.

\[
\begin{align*}
\text{ArX} + e & \rightarrow [\text{ArX}]^- \quad (9) \\
[\text{ArX}]^- & \rightarrow \text{Ar}^\cdot + X^- \quad (10) \\
\text{Ar}^\cdot + \text{Nu}^- & \rightarrow [\text{ArNu}]^- \quad (11) \\
[\text{ArNu}]^- + \text{ArX} & \rightarrow \text{ArNu} + [\text{ArX}]^- \quad (12)
\end{align*}
\]

The \(\text{S}_{\text{RN1}}\) mechanism represents a general reaction mechanism for the nucleophilic substitution of unactivated aryl halides. The order of reactivity of halides is \(I > Br > Cl > F\). Nucleophiles derived from many IVA , VA and VIA groups of elements are active nucleophilic species in the \(\text{S}_{\text{RN1}}\) mechanism.\textsuperscript{27} Amide ions, phosphite anions, arenethiolates, carbanions are examples of common nucleophiles for the substitutions by \(\text{S}_{\text{RN1}}\) mechanism.\textsuperscript{25-27} Oxygen nucleophiles were originally considered not reactive towards aryl radicals.\textsuperscript{27} Recent reports have demonstrated that both phenoxide ions\textsuperscript{28-31} and naphthoxide ions\textsuperscript{31-33} are active nucleophiles for \(\text{S}_{\text{RN1}}\). The phenoxide and naphthoxide react with aryl radicals as a carbon nucleophile (at the \textit{ortho} or \textit{para} positions of the oxygen) rather than an oxygen nucleophile.\textsuperscript{29-33}
1.1.5. Metal-Catalyzed Nucleophilic Substitutions

The nucleophilic substitution of unactivated aryl halide can also be accomplished via metal catalyzed reactions. The most prominent reactions are the copper catalyzed nucleophilic substitutions, the Ullmann etherification reactions (eq 13). Copper catalyzed reactions have been used extensively both in the laboratories and on an industrial scale.\textsuperscript{34-36} The Ullmann reactions were traditionally catalyzed by a variety of copper species with copper in the 0, +1, +2, or even +3 oxidation states including copper metal, oxides, salts, alloys, and complexes, etc. It has been recently demonstrated that copper (I) salts are the active species, the copper (II) salts are reduced to copper (I) by the nucleophile.\textsuperscript{37,38} The nucleophiles used in these reactions include nitrogen, oxygen, sulfur, halide, phosphorus, and carbon nucleophiles.\textsuperscript{36} Ullmann reactions are usually carried out in pyridine, 2,4,6-collidine, quinoline, hexamethylphosphoramide, bis(2-methylethyl)ether (diglyme), etc.\textsuperscript{36} The yield of the product by the Ullmann reaction is strongly influenced by the nature of the solvents, for example, for the same reaction product of 74% yield was obtained in pyridine versus less than 20% yield in 2,4,6-collidine.\textsuperscript{39}

\[
\text{ArX} + \text{Nu}^- \xrightarrow{\text{Cu}} \text{ArNu} + \text{X} \quad (13)
\]

In spite of the wide application of copper catalyzed reactions, the actual mechanism is still not elucidated.\textsuperscript{36,38} For the reactions using copper bonded nucleophiles (i.e. copper phenolate), the reaction exhibits a second order kinetics, first order on both the aryl halide and the copper compound. For the reactions in
which copper is used as a catalyst, the reactions are first order on aryl halide, first order on copper catalyst, and a fractional order (between 0 and 1) on the nucleophile.\textsuperscript{37,38} The substitution with electron-donating groups on the aryl halide deactivates the aryl halide, while the electron-withdrawing group such as a second halide substituent activates the aryl halide.\textsuperscript{40,41} The yield of diphenyl ether products obtained from bromobenzene and substituted phenols increases with increasing electron density at the phenolic oxygen.\textsuperscript{41} The ring substituent effects indicate the reaction constant $\rho$ ranging from +0.1 to +1.1 (the $\rho$ for $\text{S_NAr}$ reactions is 3 - 5\textsuperscript{2,3}). This suggests that the Ullmann reaction has some of the character of the $\text{S_NAr}$ mechanism. However, the order of the leaving group is $\text{I} \sim \text{Br} > \text{Cl} >> \text{F}$,\textsuperscript{40} which is in the opposite trend for the $\text{S_NAr}$ mechanism but in the same order for the $\text{S_{RN1}}$ mechanism.

At the present, the actual mechanism of the Ullmann etherification reaction is not known. This is largely due to the lack of the understanding of the nature of the interaction of cuprous ion with either the aromatic ring or the leaving group. Many mechanisms have been suggested based on the experimental evidence.\textsuperscript{35,36} They all assume that the active nucleophile is the CuNu formed from the cuprous salt and the nucleophile.

The possibility of $\text{S_{RN1}}$ mechanism was previously ruled out based on the following series of experimental results. The copper (I) catalyzed reaction was not affected by the additions of radical or electron traps.\textsuperscript{42,43} The copper catalyzed reaction of $p$-chloroiodobenzene with thiophenolate led to the monosubstituted product,\textsuperscript{42} while an $\text{S_{RN1}}$ reaction should yield the disubstituted product.\textsuperscript{25-27} However, radical species was recently detected in the polymerization of Cu(I) 4-
bromobenzenethiolate.\textsuperscript{44} The $S_{RN1}$ mechanism was consequently proposed for the polymerization reaction.\textsuperscript{44}

The following mechanisms are proposed as working hypotheses for guiding the design of the reactions. The $\pi$-complex mechanism was initially proposed by Weingarten\textsuperscript{37} and subsequently refined by Paine and Couture.\textsuperscript{38,43} In this mechanism (eq 14), an 18-electron $\pi$-complex was formed between the CuNu and the 6 $\pi$-electrons of the aromatic ring. The intramolecular attack of the nucleophile from CuNu at the ipso position of the leaving group results in a tetrahedral complex. It was assumed that the "negative charge" was neutralized by the $\pi$-complexed copper atom. This explains the lack of para-substituent effects in the Ullmann reaction. The rate-determining step was assumed to be the release of the halide, which accordingly should lead to the observed reactivity order of I > Br > Cl > F due to the C-X bond strength. The mechanism can also account for the observed retardation effects of added salts.\textsuperscript{43} The addition of salts causes the formation of copper species with two ligands which are incapable of forming the 18-$\pi$-electron complex which is required to facilitate the nucleophilic substitution.

\[
\begin{align*}
\text{ArX} + \text{CuNu} & \rightleftharpoons \text{CuNu} \rightarrow \text{Cu} \rightarrow \text{ArNu + CuX} \\
\text{ArNu} & \rightarrow \text{Nu} \rightarrow \text{ArNu} + \text{CuX} \quad (14)
\end{align*}
\]

The other mechanism suggested for the Ullmann reaction involves Cu(III) species\textsuperscript{36,42,45} (eq 15). Copper (I) with a 3d\textsuperscript{10} configuration undergoes oxidative
addition by an inner sphere electron transfer leading to copper (II) in the transition state. It subsequently rearranges to copper (III) by an intramolecular halide migration. The substitution product is formed by the reductive elimination of the copper halide.

\[
\begin{align*}
\text{ArX} + \text{CuNu} & \rightarrow [\text{Ar-X- Cu(II)Nu}]^\pm \\
& \rightarrow \text{Ar- Cu(III)Nu} \rightarrow \text{ArNu} + \text{CuX} \quad (15)
\end{align*}
\]

\[
\begin{align*}
\text{ArX} + \text{M(0)L}_2 & \rightarrow \text{Ar-M(II)X} \quad (16)
\end{align*}
\]

\[
\begin{align*}
\text{Ar-M(II)X + Nu}^- & \rightarrow \text{Ar-M(II)Nu} + X^- \quad (17)
\end{align*}
\]

\[
\begin{align*}
\text{Ar-M(II)Nu} & \rightarrow \text{ArNu} + \text{M(0)L}_2 \quad (18)
\end{align*}
\]

\(X = \text{I, Br; } M = \text{Pd, Ni; } L = \text{PPh}_3, \text{ etc.; } \text{Nu} = \text{RS}^-, \text{ ArS}^-, \text{ etc.}\)

Besides copper, aromatic nucleophilic substitutions of unactivated aryl halides are also catalyzed by either Pd(0)\textsuperscript{46-49} or Ni(0).\textsuperscript{50,51} These reactions do not proceed by S\textsubscript{RN1} mechanism since they are not retarded by the S\textsubscript{RN1} inhibitors.\textsuperscript{46} The nucleophiles are thiolate anions, enolate anions of acetophenone, and cyanide anions.\textsuperscript{46} Reactions are performed usually in N,N-dimethylformamide (DMF),
dimethyl sulfoxide (DMSO), or N-methylpyrrolidinone (NMP). The reaction mechanism consists of the oxidative addition of M(0)L₂ to aryl halide (eq 16), the subsequent nucleophilic substitution of the M(II) activated aryl halide ArML₂X by the nucleophile (eq 17), and the reductive elimination of the metal catalyst leading to the substitution product (eq 18). However, the synthesis of asymmetric substitution product has the by-products resulting from the trans-substitutions.⁵⁰

1.2. MECHANISMS OF AROMATIC ELECTROPHILIC SUBSTITUTIONS

Aromatic electrophilic substitution reaction occurs by the attack of an electrophile on the aromatic ring. There are three classes of electrophiles with different reactivities: 1) strong electrophiles capable of reacting with deactivated aromatic rings (i.e. containing electron-withdrawing groups) which include NO₂⁺, SO₃, RSO₃⁺, Br₂ and Cl₂, etc.; 2) electrophiles capable of reacting with benzene or activated aromatic substrates (i.e. substituted with electron-donating groups) which include carbocations, acylium ions, protons, etc.; 3) weak electrophiles, such as diazonium ions, which react only with the activated aromatic compounds. The group to be substituted is usually a proton. However, branched alkyl groups, halogens, and silyl groups can also be substituted.⁵²⁵³ The electrophilic substitutions are usually catalyzed by Lewis acids, such as AlCl₃, FeCl₃, TiCl₄, etc. In spite of the broad scope of the electrophilic substitution of aromatic compounds, the majority of the reactions proceeds by just one mechanism, i.e. the arenium mechanism.
1.2.1. The Arenium Mechanism

The arenium mechanism is also termed as the $S_{E2}$ or the $\sigma$-complex mechanism. The electrophile $E1^+$ attacks the aromatic ring to form the tetrahedral Wheland complex, i.e. the arenium ion (eq 19). The forward reaction of eq 19 is usually the rate-determining step. The arenium has only 4 delocalized $\pi$-electrons and therefore subsequently eliminates a proton leading to the substitution product (eq 20). Electrophilic substitution can also be effected by the attack of the positive end of a dipole.\(^2\)

\[
\begin{align*}
\ce{Ar-X + E1^+ &<=> [X \text{ Arenium Ion}]_{E1}} \\
\ce{[X \text{ Arenium Ion}]_{E1} \rightarrow [X \text{ Arenium Ion}]_{E1} + X^+} \\
\ce{ArH + NO2^+ &<=> [ArH^+ NO2^- \text{ Charge Transfer Complex}]^{-}} \\
\ce{[ArH^+ NO2^- \text{ Charge Transfer Complex}]^{-} \rightarrow [ArH^+ NO2^- \text{ Arenium Ion}]^{-}}
\end{align*}
\]

A single electron transfer (SET) mechanism was proposed for the formation of the arenium ion in the nitration of aromatic compounds more reactive than toluene.\(^{54,55}\) The mechanism (eq 21) involved a diffusion-controlled SET between $\ce{ArH}$ and $\ce{NO2^+}$ leading to a radical pair, which subsequently collapses to the usual arenium ion.

1.2.2. The $S_{E1}$ Mechanism

The $S_{E1}$ mechanism is the opposite of the $S_{N1}$ mechanism in the nucleophilic substitutions (Section 1.1.1). The cleavage of the C-X bond leads to a
phenyl anion (eq 22), the resulting phenyl anion undergoes electrophilic reaction with the electrophile (eq 23). The S_{E1} mechanism operates only in a few special reactions, such as the decarbonylation of an aromatic aldehyde and the copper catalyzed decarboxylation reactions of aromatic carboxylic acids.²

\[
\begin{align*}
\text{Ph}^+ \quad \text{X} \quad \text{Ph}^- & \quad \text{(22)} \\
\text{Ph}^- \quad + \quad \text{El}^+ \quad \rightarrow \quad \text{Ph}^- \quad \text{El} & \quad \text{(23)}
\end{align*}
\]

1.3. CONVENTIONAL SYNTHESIS OF AROMATIC POLYETHERS

Aromatic polyethers are important high performance engineering plastics. These polymers are frequently synthesized by the variants of both the aromatic nucleophilic substitution and electrophilic substitution reactions. Typical engineering plastics synthesized by these techniques include aromatic poly(ether sulfones)s,⁵⁶,⁵⁷ poly(ether ether ketone)s (PEEK),⁵⁸-⁶⁰ poly(ether ketone)s (PEK),⁵⁸-⁶⁰ and poly(ether imide)s.⁶¹-⁶³

The conventional synthesis of poly(2,6-dimethyl-1,4-phenylene oxide) (PPO) is by the oxidative polymerization of 2,6-dimethylphenol by oxygen, in the presence of a copper-amine complex as catalyst.⁶⁴-⁷¹

1.3.1. Synthesis of Aromatic Polyethers by Aromatic Nucleophilic Substitutions

The aromatic nucleophilic substitutions of an aryl dihalide containing either sulfonyl or carbonyl groups with a difunctional nucleophile lead to poly(ether
sulfones and poly(ether ether ketone)s. These reactions occur by an \( S_NAr \) mechanism (eq 24).\(^{56-60}\) The diaryl dihalides are activated by the electron-withdrawing SO\(_2\) or CO groups. Since the reactivity of halides follows \( F \gg Cl > Br > I \), the halogens of the dihalides activated by a SO\(_2\) group can be either F or Cl. However, for the CO activated dihalide only F can be substituted to high molecular polymers due to the weaker electron-withdrawing capability of the CO group versus that of SO\(_2\) group.

\[
\begin{align*}
n \text{X-Ar-Y-Ar-X} + n \text{MO-Ar'-OM} & \longrightarrow \quad \text{O-Ar'-O-Ar-Y-Ar} \quad (24) \\
n \text{MO-Ar-Y-Ar-X} & \longrightarrow \quad \text{O-Ar-Y-Ar} \quad (25)
\end{align*}
\]

\( Y = \text{SO}_2, X = \text{Cl, F} \)
\( Y = \text{CO, X = F} \)
\( M = \text{K, Na} \)

The difunctional nucleophile (eq 24) is usually a bisphenolate. Various bisphenols are used such as 2,2-bis(4-hydroxy-3,5-dimethylphenyl)propane (Bisphenol A), \( p \)-hydroquinone, and 4,4'-biphenol. The polymerizations are usually carried out in high-boiling, dipolar aprotic solvents such as DMF, DMSO, N,N-dimethylacetamide (DMAc), N-methylpyrrolidino (NMP), sulfolane, diphenyl sulfone, etc.\(^{57,60}\) The dipolar aprotic solvents enhance the effective solubility of the phenol by solvating the counter-cation. The counter-cation is usually K or Na. The phenolate salts are commonly generated \textit{in situ} by azeotropic distillation of the water by-product from a solution of the phenol and the base (usually sodium or potassium hydroxide or potassium carbonate). The
polymerizations are performed at temperatures high enough to maintain the bisphenolates dissolved in the organic phase ($\geq 160^\circ$C) and under an inert atmosphere (nitrogen or argon). Polymers of similar structure can also be synthesized by the self-polyetherification of a monomer containing both a halide and a phenol group (eq 25).

Poly(ether ether ketone)s (PEEK) crystallize easily from the polymerization solution. The high molecular weight PEEK is synthesized only in diphenyl sulfone or benzophenone at a temperature close to the melting point of the polymer, i.e. about 335°C. Several variants of the synthetic scheme (eqs 24 and 25) have been developed, such as the substitution of nitro groups instead of halides and the use of trimethylsilyl derivative of the phenol to improve the reactivity.\textsuperscript{57, 60, 62, 72}

1.3.2. Synthesis of Aromatic Polyethers by Aromatic Electrophilic Substitutions

Aromatic poly(ether sulfone)s and poly(ether ketone)s (PEK) are synthesized by Friedel-Crafts polysulfonylation and polyacylation reactions.\textsuperscript{56-60} The monomers are usually aromatic disulfonyl halides and a aromatic compounds with an ether linkage (eq 26). These polymerizations requires a large amount of Lewis acid catalyst (at least one mole catalyst per mole of aromatic electrophile and heteroatom). AlCl$_3$, FeCl$_3$, SbCl$_5$, and BF$_3$/HF are effective catalysts for their synthesis. The reactivity of AlCl$_3$ is modified by the addition of a Lewis base.\textsuperscript{63} High temperatures accelerate the polymerization but also result in side reactions at the less reactive positions. The side reactions between the aromatic rings and the Lewis acid occur at high catalyst concentrations. The common problems with the synthesis using two monomers (eq 26) is the deactivation of the aromatic monomer
after monosubstitution by an electron-withdrawing group. This problem is overcome by the self-polymerization approach similar to eq 25.

\[
\begin{align*}
n \text{XY-Ar-YX} + n \text{HAr'H} & \rightarrow \frac{\text{Ar'-Y-Ar-Y}}{n} \\
n \text{HOOArYOH} + n \text{HAr'H} & \rightarrow \frac{\text{Ar'-Y-Ar-Y}}{n}
\end{align*}
\] (26)

\[
Y = \text{SO}_2, \text{CO} \\
X = \text{Cl}
\]

Reaction variants using arenedisulfonic acid or aryl dicarboxylic acids were developed (eq 27). These polymerizations can be performed directly with dicarboxylic acids at lower temperatures in the presence of a drying agent and a strong acid such as methanesulfonic acid.\textsuperscript{60} or triflic acid.\textsuperscript{73}

1.3.3. Conventional Synthesis of Poly(2,6-Dimethyl-1,4-Phenylene Oxide) (PPO)

\[
\begin{align*}
n \text{H} & \text{C} \text{O} \text{H} + \frac{n}{2} \text{O}_2 \xrightarrow{\text{Cu-Amine}} \frac{\text{H} \text{C} \text{O}}{n} \\
+ \text{H} & \left[ \text{H} \text{C} \text{O} \text{H} \right]_{n} \rightarrow \frac{\text{H} \text{C} \text{O} \text{H} \text{C} \text{O} \text{H}}{n} + \frac{\text{NR}_2}{n}
\end{align*}
\] (28)

The conventional synthesis of PPO is based on the oxidative polymerization of 2,6-dimethylphenol by a stoichiometric amount of oxygen catalyzed by a copper-amine complex.\textsuperscript{64-71} This polymerization was discovered by Hay and co-workers
in 1959 at the General Electric (eq 28). The PPO has a glass transition temperature of 205-210°C. The melting temperature of crystalline PPO is 262-267°C. The polymer has excellent thermal, oxidative, dimensional, and hydrolytic stability. The polymer has been used extensively for both industrial and commodity applications.

The proposed mechanism of this polymerization is based on the radical-radical coupling of the phenoxy radicals (Scheme 1.1). The oxidation of 2,6-dimethylphenol (1) yields its phenoxy radical 5. The C-O coupling of two phenoxy radicals 5 forms a quinone ether 6, which may either dissociate back to the two starting radicals or enolize to a dimer phenol 7 (eq 29). The dimer phenol 7 is subsequently oxidized to its dimer phenoxy radical 8, which also couples with a monomer radical 5 leading to a trimer phenol 10 by enolization (eq 30). All the propagation steps are reversible (eqs 29 and 30). The coupling between two oligomeric or polymeric radicals causes a redistribution reaction (eq 31). The redistribution between two dimer radicals 8 generates a quinol ether which may dissociate into a monomer radical 5 and a trimer radical 12. This polymerization follows a molecular weight versus conversion relationship of the "reactive intermediate polycondensation".

The difunctional polymer PPO-2OH 3 results from the carbon-carbon coupling of the phenoxy radical 5 at its 4 position yielding 3,3',5,5'-tetramethyl-4,4'-diphenoquinone 13 (eq 32). Typically, about 3% of 13 results from the polymerization of 2,6-dimethylphenol. The diphenoquinone 13 subsequently couples with the phenoxy radical 5 leading to the PPO-2OH of structure 3 (eq 33).
Scheme 1.1. The radical-radical coupling mechanism of the polymerization of 2,6-dimethylphenol.
The PPO synthesized by this polymerization method exhibits usually a bimodal and broad molecular weight distribution. Most of the PPO has the structure of 2 (eq 28), i.e. PPO with one 2,6-dimethylphenol chain end (PPO-OH). However, this PPO also contains a low content of polymer containing two phenol chain ends (PPO-2OH) of structure 3 and structure 4 (eq 28) with the methyl group substituted with dialkylamino groups (from the amine catalyst) as demonstrated by the $^{13}$C-NMR studies. These minor components can not be removed by purification due to their high molecular weights. Since macromonomers and telechelics must have absolute functionalities. The presence of both PPO-OH and PPO-2OH makes it impossible to use the PPO obtained by conventional synthesis as precursor for the synthesis of both classes of chain ended functional PPOs.

1.4. SYNTHESIS OF AROMATIC POLYETHERS
BY ION-RADICAL POLYMERIZATIONS

This dissertation is concerned with the development of novel synthetic approaches to the synthesis of aromatic polyethers, including poly(2,6-dimethyl-1,4-phenylene oxide)s, aromatic poly(ether sulfone)s, poly(ether ether ketone)s, and fully aromatic polyethers by ion-radical polymerization reactions.
1.4.1. Synthesis of PPO by an Anion-Radical Polymerization

There are three different approaches to the anion-radical polymerization of 4-bromo-2,6-dimethylphenol.\textsuperscript{77-81} The first approach was developed by Staffin and Price.\textsuperscript{77} 4-Bromo-2,6-dimethylphenol is polymerized at the interface between the benzene and aqueous alkaline phases. This polymerization was initiated by a catalytic amount of initiator such as lead dioxide or potassium ferricyanide. These initiators are oxidants which oxidize the phenol to its phenoxy radical. The polymers are proposed to be formed by an anion-radical polymerization (similar to Scheme 1.2 in the propagation step).\textsuperscript{77} Although the resulting polymers are monofunctional when the polymerization is performed in air, the anion-radical mechanism of polymerization is complicated by the results from the polymerizations performed under nitrogen,\textsuperscript{78} which led to uncontrollable functionality and extensive branching. These results suggest that the polymerization has radical-radical propagation (similar to Scheme 1.1) as a side reaction which causes the branching of the polymers.\textsuperscript{78} The radical-radical propagation is facilitated by the high radical concentration in the organic phase and the low availability of the monomer phenolate only at the organic/aqueous interface. Due to this aspect of the reaction, the chain termination is irreversible since no efficient deprotonation of the polymer phenol chain end is possible due to the limited access to the interface.

The second approach is an organic phase polymerization of 4-bromo-2,6-dimethylphenol.\textsuperscript{79,80} The polymerization is initiated by similar copper-amine catalyst as in the oxidative polymerization of 2,6-dimethylphenol. However, 4-bromo-2,6-dimethylphenol is polymerized with a catalytic amount of the preformed copper-amine catalyst. The polymerization in pyridine without added base is slow
and requires an elevated temperature (60°C). The use of potassium tert-butoxide allows room temperature polymerization.

The third approach is based on the phase transfer catalyzed (PTC) organic phase/aqueous alkaline phase polymerization of 4-bromo-2,6-dimethylphenol (eq 34).81 This polymerization is performed in open air with only a catalytic amount (5 mol% versus phenol) of a phase transfer catalyst such as tetrabutyl ammonium hydrogen sulfate. The polymerization leads to PPO polymer with a 4-bromo-2,6-dimethylphenoxy and a 2,6-dimethylphenol chain ends, i.e. PPO-OH.82 The PPO-OH synthesized by this PTC polymerization has been used as precursor for the synthesis of PPO macromonomer.82

\[
\begin{align*}
\text{nBr} & \quad \text{OH} & \quad \text{Bu}_4\text{NHSO}_4, \text{air} & \quad \text{C}_6\text{H}_6/\text{NaOH (aq)} & \quad \text{Br} & \quad \text{O} & \quad \text{H} \\
\text{13} & & & & \text{14} & & (34)
\end{align*}
\]

This polymerization was proposed to proceed by an anion-radical mechanism (Scheme 1.2). During the polymerization, the monomer phenolate 15 is formed as the phenol monomer 13 is dissolved in the aqueous NaOH solution. The phase transfer catalyst complexes with the phenolate 15 to form a phenolate with an onium counter-cation 16 (eq 35). 16 is lipophilic and is transferred to the organic phase as 17 (eq 36). In the non-polar organic phase (benzene or toluene), the ion-pair 17 is not solvated and therefore is activated toward oxidation. Oxygen from trace of dissolved air oxidizes 17 to its corresponding phenoxy radical 18 (eq 37). The role of air has been demonstrated to be crucial to the polymerization. This polymerization is negligible when the amount of available air is reduced but not eliminated.78,81
Scheme 1.2. The anion-radical mechanism proposed for the PTC polymerization of 4-bromo-2,6-dimethylphenol.
The propagation consists of the radical nucleophilic substitution at the ipso position of the bromo substituent of a phenolate monomer 17 (eq 38), since it has been demonstrated that both phenolates and naphtholates act as carbon nucleophiles but not oxygen nucleophiles.\textsuperscript{29-33} The ipso attack represents the only possible position since both ortho positions of the phenolate are substituted with methyl groups. The anion-radical 19 eliminates a bromide to form a dimer phenoxy radical 20 (eq 39). By the same radical nucleophilic addition a polymeric phenoxy radical 21 is resulted (eq 40).

This polymerization proceeds by a chain reaction, however the chain propagation takes place by the a substitution type reaction. The major difference between this polymerization and the oxidative polymerization of 2,6-dimethylphenol (Section 1.3.3) is the concentration of the phenoxy radical. This polymerization has a low concentration of the phenoxy radical since the chain initiation is a rate-determining step as limited by the low concentration of dissolved air in the organic phase. In contrast, the conventional PPO synthesis uses a stoichiometric amount of oxygen and leads to very high concentration of phenoxy radical. The high concentration of the phenoxy radical results in the undesired C-C coupling. Therefore, the PTC polymerization does not have C-C coupling as quantitatively demonstrated.\textsuperscript{82}

The termination step yields a phenol chain end 14 (eq 41). Under PTC conditions, the PPO-OH 14 can be deprotonated either by the phenolate monomer 17 in the organic phase (eq 42) or by the tetrabutylammonium hydroxide (eq 43). The deprotonated polymer chain end 22 can be subsequently oxidized to its phenoxy radical 21 (eq 44). Therefore under PTC conditions the termination reaction is reversible.
The PTC anion-radical polymerization partially resembles the $S_{RN1}$ mechanism (Section 1.1.4). The propagating species is a free radical and the propagation involves also an anion-radical intermediate.\textsuperscript{24-27} In contrast to $S_{RN1}$ reaction, the initiation of a propagating chain requires a single electron oxidation of the phenolate while the $S_{RN1}$ requires single electron transfer reduction of the aromatic substrate. The propagation of this polymerization proceeds by the phenoxy radical while the $S_{RN1}$ proceeds by an aryl radical. Further the propagation has the halide elimination leading to new radical which does not involve a single electron transfer with the substrate as in the $S_{RN1}$. Therefore this anion-radical polymerization does not proceed by a conventional $S_{RN1}$ mechanism. The mechanism is a variant of the conventional $S_{RN1}$ mechanism. Polymerization by the conventional $S_{RN1}$ mechanism has been recently reported for the synthesis of poly(p-phenylene sulfide) from 4-bromothiophenolate.\textsuperscript{44,83,84}

The anion-radical polymerization also resembles the initiation step of the $S_{ON2}$ (bimolecular oxidative nucleophilic substitution) mechanism\textsuperscript{85-88} in the sense that both are initiated by a single electron oxidation. However, the $S_{ON2}$ propagation proceeds by a cation-radical rather than a radical as in the anion-radical polymerization.

It should also be noted that the propagation of both the dimeric phenoxy radical 20 and the polymeric phenoxy radical 21 is fast than the monomeric phenoxy radical 18. This is due to the monomeric phenoxy radical 18 has lower reactivity towards propagation since the phenoxy radical is resonance stabilized by the $p$-bromo substituent. This results in the molecular weight-conversion dependence for this PTC polymerization to be different from both the step-growth and the chain-growth polymerizations. Polymers of intermediate molecular weights
Figure 1.1. The dependence of number average molecular weight ($M_n$) on the conversion for different polymerization reactions.\textsuperscript{74}
of about 4000 g/mol are obtained at about 5-10% conversion.\textsuperscript{81} This type of polymerization has been classified by Heitz as "reactive intermediate polycondensation" (Figure 1.1).\textsuperscript{74} Therefore low molecular weight PPO-OH can only be obtained by stopping the polymerization at low conversions. It is in fact impossible to synthesize PPO-OH with controlled molecular weights over a wide range of number average molecular weights. PPO-OH polymers with a wide range of molecular weights was previously obtained by exhaustive fractionation of the PPO-OH synthesized by the PTC polymerization.\textsuperscript{82}

In Part I of this dissertation, various techniques developed to overcome these problems in the PTC synthesis of PPO-OH are presented. This approach consists of the phase transfer catalyzed anion-radical copolymerization of 4-bromo-2,6-dimethylphenol with various comonomeric phenols. Convenient polymerization methods were developed to synthesize PPO with both controlled molecular weights and controlled functionalities (either PPO-OH or PPO-2OH). These accomplishments offer an easy and efficient synthesis of PPO-OH precursors for the synthesis of PPO macromonomers.

Chapter 2 describes the PTC polymerization of 4-bromo-2,6-dimethylphenol in the presence of either 2,4,6-trimethylphenol or 4-\textit{tert}-butyl-2,6-dimethylphenol. These PTC copolymerizations lead to the synthesis of PPO-OH with conveniently controlled molecular weights and narrow polydispersities at satisfactory yields. The anion-radical mechanisms for both the molecular weight control and the side reactions associated with the 2,4,6-trimethylphenol are discussed.

The first part of Chapter 3 presents the synthesis of PPO-2OH by a PTC copolymerization of 4-bromo-2,6-dimethylphenol with a bifunctional phenol, i.e.
2,2-bis(4-hydroxy-3,5-dimethylphenyl)propane. The second part of Chapter 3 describes both the homopolymerization of a phenol with an alcohol functionality and the copolymerization of the phenol with 4-bromo-2,6-dimethylphenol. The phenol is 4-hydroxy-3,5-dimethylbenzyl alcohol. This study was intentionally studied to confirm the suggestion that this phenol is not involved in the PTC copolymerization with 2,4,6-trimethylphenol.

The investigations to control the molecular weights of PPO by a PTC copolymerization of 4-bromo-2,6-dimethylphenol with a terminating phenol comonomer are described in Chapter 4. Two sterically hindered phenols which can not self-propagate are selected to demonstrate this idea.

Chapter 5 deals with the PTC depolymerization of high molecular weight PPO-OH in the presence of either 2,4,6-trimethylphenol or 4-tert-2,6-dimethylphenol. These depolymerization reactions proceed by an anion-radical mechanism. These results have conclusively demonstrated the redistribution reaction between a phenoxy radical and a polymeric phenolate which corresponds to the redistribution reaction during the polymerization.

1.4.2. Synthesis of Aromatic Polyethers by Cation-Radical Polymerization

The conventional synthesis of poly(ether sulfone)s, poly(ether ether ketone)s uses drastic polymerization conditions (Sections 1.3.1 and 1.3.2), which are usually performed at high temperatures in expensive dipolar aprotic solvents. These synthetic methods also frequently involves the slow process of azeotropic removal of water formed from the reaction mixture. In Part II of this dissertation, alternative polymerization methods are developed for the synthesis of poly(ether
sulfone)s, poly(ether ether ketone)s and fully aromatic polyethers. These polymerization reactions are performed at room temperature in non-dipolar aprotic solvents. FeCl₃ is used as a Lewis acid oxidant. This polymerization proceeds by a cation-radical mechanism.

The specific reaction used is an oxidative aromatic-aromatic coupling reaction (the Scholl reaction). The mechanism of the Scholl reaction has been demonstrated as cation-radical in nature. The single electron oxidation of a aromatic substrate generates its corresponding cation-radical. The oxidation is effected by the the treatment of the substrate with 1) Brønsted acids such as H₂SO₄; 2) oxidizing Lewis acids, e.g. FeCl₃; 3) halogens, e.g. Br₂; 4) metal salts such as Ti(CF₃COO)₃; 5) via a charge transfer complex, e.g. chloranil; 6) irradiation; 7) catalytic surface such as a zeolite; 8) electrochemical oxidation at the anode, etc.

Kovacic and co-workers have synthesized poly(1,3-phenylene)s from benzene by reactions with various Lewis acids. The polymerization of α,ω-bis(1-naphthoxy)alkanes under the Scholl conditions led to the synthesis of polyethers with both aromatic and aliphatic segments.

The synthesis of aromatic poly(ether sulfone)s and poly(ether ether ketone)s by the Scholl reaction was recently accomplished by Percec and Nava, who polymerized 4,4'-bis(1-naphthoxy)diphenyl sulfone and 4,4'-bis(1-naphthoxy)benzophenone under Scholl reaction conditions.

Part II of this dissertation presents the novel developments in the synthesis of aromatic polyethers by the Scholl reaction. The emphasis has been directed to the understanding of the polymerization mechanisms and of the factors that
determine the polymerizability of the monomers. The synthesis of several classes of novel aromatic polyethers is also investigated.

Chapter 6 is concerned with the polymerizability of 4,4-bis(phenoxo)diphenyl sulfones and 4,4'-bis(phenylthio)diphenyl sulfone. The effects of sulfur versus oxygen and the effects of substituting the two phenoxy rings of 4,4-bis(phenoxo)diphenyl sulfone with various electron-donating groups are studied. The factors that determine the polymerizability are differentiated based on both the experimental results and the mechanistic considerations.

Chapter 7 describes the cation-radical polymerization of various bis(phenoxo)pentane monomers and bis(phenylthio)pentane. The polymerization reactions of these monomers are compared with their aromatic counterparts, i.e. 4,4'-bis(phenoxo)diphenyl sulfones (Chapter 6), to provide the information about the reactivity of the monomers and the cation-radicals.

In Chapter 8, the polymerizability of 4,4'-bis(1-naphthoxy)diphenyl sulfone and 1,5-bis(1-naphthoxy)pentane is critically examined. The polymerization results present an example in which the overall polymerizability of the two monomer is determined by the reactivity of the growing cation-radical species. The mechanistic conclusion is also supported by difference in the selectivity of the two growing species.

Chapter 9 presents the cation-radical homopolymerization and copolymerization of monomers containing perfluoroalkyl segments. The copolymerization experiments offer information as to the effect of the reactivity of the comonomers on the composition of the resulting copolymers.

Chapter 10 is concerned with the synthesis and cation-radical polymerization of a series of monomers with central phenylene rings substituted
with either one methylene, two ketone groups, or two methylene groups. The effects of the electron-withdrawing groups versus electron-donating groups on the polymerizability are demonstrated.

Chapter 11 presents the synthesis and the cation-radical polymerization of various fully aromatic ether monomers. Previously high molecular weight fully aromatic polyethers were reportedly synthesized only by the Ullmann reaction at temperatures above 200°C.\textsuperscript{100,101} In contrast, the synthesis of fully aromatic polyethers by cation-radical polymerization is performed at room temperature. The cation-radical polymerization of 2,2-bis(4-hydroxy-3,5-dimethylphenyl)propane is also described in this chapter, electrophilic transalkylation reactions are observed under the cation-radical reaction conditions.

1.4.3. Reactivity of Macromonomers

Part III of this dissertation is concerned with the investigation of \( \omega -(p\text{-vinylbenzyl}) \) ether macromonomer of PPO (PPO-VBE).

Macromonomers are oligomers or polymers having a homopolymerizable groups.\textsuperscript{102-107} The polymerizable groups include vinyl, acetylene, acrylate and heterocycle groups. The interest in macromonomers comes from their application in the synthesis of well-defined graft copolymers. Since the macromonomers can be synthesized to have controlled molecular weights and narrow polydispersities, the copolymerization of a macromonomer with a comonomer represents the most convenient and reliable approach to control the graft length of the resulting graft copolymers. However, the control of the main chain sequence length requires the knowledge on the reactivity of the macromonomers.\textsuperscript{105-107}
The reactivity of macromonomers should be molecular weight independent. However, the reported results have demonstrated that the reactivity of the macromonomer is molecular weight dependent,\textsuperscript{82,108-110} or even conversion dependent.\textsuperscript{108,111} The nature of the polymerization solvent was also reported to influence the reactivity of the macromonomer.\textsuperscript{112}

Chapter 12 presents the study on the effects of various polymerization conditions on the determined "reactivity" of PPO-VBE macromonomers. Both the macromonomer concentration and the nature of the polymerization solvents are studied for PPO-VBE macromonomer in free radical copolymerization with methyl methacrylate. These results demonstrate that the non-ideality of the polymerization mixture, such as micelle formation during the polymerization, affects the determination of the reactivity of the macromonomer.

1.5. GENERAL EXPERIMENTAL TECHNIQUES

200 MHz $^1$H-NMR spectra were recorded on a Varian XL-200 spectrometer. The spectra were obtained in either CCl$_4$, CDCl$_3$, acetone-d$_6$, or dimethyl sulfoxide-d$_6$ solutions with TMS as internal standard. The spectra were taken either at room temperature or at elevated temperatures.

The relative 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 five PL-gel columns of $10^2$, $5 \times 10^2$, $10^3$, $10^4$, and $10^5$ Å or a set of two PL-gel columns of $5 \times 10^2$ and $10^4$ Å are used for the determinations. Either
tetrahydrofuran (THF) or chloroform were used as solvents for GPC at 1 mL/min. The calibration plots of both sets of columns were constructed with polystyrene standards (Supelco). Purity of all compounds was similarly determined by high performance liquid chromatography (HPLC) using a 100 Å PL-gel column.

A Perkin-Elmer DSC-4 differential scanning calorimeter, equipped with a TADS 3600 data station, was used to determine the glass transition temperatures of the polymers at a heating rate of 20°C/min. The glass transition temperatures were read at the middle of the change in the heat capacity of the second DSC heating scan.

REFERENCES


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PART I
SYNTHESIS OF AROMATIC POLYETHERS
BY PHASE TRANSFER CATALYZED
ANION-RADICAL REACTIONS
CHAPTER 2

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

2.1. INTRODUCTION

Oligomers, macromonomers and telechelic polymers are of interest both from the fundamental and the applied points of view. Oligomers are synthesized as model compounds for elucidating polymerization mechanisms and for predicting the physical properties of polymers. In contrast, macromonomers and telechelics are structural precursors for the synthesis of new polymers and sequential copolymers.\textsuperscript{1-3} In many step polymerizations, both molecular weight and chain end functionality can be controlled by well established procedures. However, neither are well controlled in "reactive intermediate polycondensations."\textsuperscript{1-8}

Polymerization of either 2,6-dimethylphenol\textsuperscript{4,5-9} or 4-bromo-2,6-dimethylphenol\textsuperscript{5-10} follows a "reactive intermediate polycondensation" mechanism\textsuperscript{4,10,12} There are several synthetic procedures to obtain poly(2,6-dimethyl-1,4-phenylene oxide) with two 2,6-dimethylphenol chain ends (PPO-2OH)\textsuperscript{4,9,12-14} Surprisingly, it is only possible to synthesize poly(2,6-dimethyl-1,4-phenylene oxide) with well defined molecular weights and with only one 2,6-dimethylphenol chain end (PPO-OH) by oxidative polymerization if the polymerization is stopped at low conversion.\textsuperscript{9-11,15} When the oxidative polymerization of 2,6-dimethylphenol is carried to high conversion, a small quantity
of 3,3',5,5'-tetramethyl-4,4'-diphenoquinone is also formed, which initiates polymerization in two directions, thereby resulting in low concentrations of PPO-2OH.\textsuperscript{11-14}

The most convenient synthesis of PPO-OH is by phase transfer catalyzed polymerization of 4-bromo-2,6-dimethylphenol.\textsuperscript{10,11} This reaction represents a development of the polymerization of 4-bromo-2,6-dimethylphenol in a two-phase system with an oxidizing agent.\textsuperscript{8} The similarities and differences between these two polymerization procedures were previously described in detail.\textsuperscript{10} In the phase transfer catalyzed polymerization process the molecular weight of the resulting PPO-OH is conversion dependent.\textsuperscript{10} Because PPO-OH is a synthetic precursor of macromonomers with various homopolymerizable groups,\textsuperscript{11} a synthetic method to prepare perfectly monofunctional PPO-OH of well defined molecular weight at high conversion is particularly desirable.

This chapter describes a synthetic procedure based on the phase transfer catalyzed polymerization of 4-bromo-2,6-dimethylphenol in the presence of either 2,4,6-trimethylphenol or 4-\textit{tert}-butyl-2,6-dimethylphenol. Although 2,4,6-trimethylphenol also controls the molecular weight of PPO synthesized by the oxidative polymerization of 2,6-dimethylphenol,\textsuperscript{7,16,17} it is not certain whether the resulting polymers consist of pure PPO-OH or a mixture of PPO-OH and PPO-2OH.

\section*{2.2. EXPERIMENTAL}

\subsection*{2.2.1. Materials}

4-Bromo-2,6-dimethylphenol (97\%, Aldrich) was recrystallized from petroleum ether, m.p.: 78-79°C. 2,4,6-Trimethylphenol (99\%, Aldrich),
tetrabutylammonium hydrogen sulfate (TBAH) (97%, Aldrich) and all other reagents were used as received or purified by standard methods.

Synthesis of 4-tert-butyl-2,6-dimethylphenol (1')

4-t-Butyl-2,6-dimethylphenol (1') was synthesized by a modification of a literature procedure.\textsuperscript{18} \( \text{H}_2\text{SO}_4 \) (72\%, 236 g) was added dropwise to a mixture of 2,6-dimethylphenol (71 g, 0.58 mol) and t-butanol (72 g, 0.72 mol), and the reaction mixture was stirred at 60 °C for 4 h. Three portions of diethyl ether were used to extract the reaction mixture. The ether extracts were then washed with saturated \( \text{NaHCO}_3 \) and water, and dried with anhydrous \( \text{CaCl}_2 \). Ether was removed on a rotovapor. The residue was recrystallized from petroleum ether to yield 70 g (68\%) white crystals, m.p.: 78-80 °C; \( ^1\text{H}-\text{NMR (CDCl}_3, \text{TMS, 25}^\circ\text{C}): 1.28 \text{ ppm (s, 9H, (CH}_3\text{)}_3\text{C}-, 2.25 \text{ ppm (s, 6H, Ar-CH}_3\text{), 4.46 ppm (s, 1H, Ar-OH), 7.00 ppm (s, 2H, Ar-H).} \)

2.2.2. Polymerization Experiments

Phase Transfer Catalyzed Homopolymerization of 2,4,6-Trimethylphenol (1)

2,4,6-Trimethylphenol (1, 0.500 g, 3.68 mmol) was dissolved in 5 N aqueous NaOH (7.5 mL). Benzene (7.5 mL) and TBAH (0.063 g, 0.0168 mmol) were added, and the reaction mixture was stirred for 24 h at room temperature in the presence of air. The reaction was quenched by neutralizing with cold 1.5 N HCl. The benzene layer was separated, washed with distilled water, and dried with anhydrous \( \text{CaCl}_2 \). Benzene was evaporated on a rotovapor to yield a residue, which crystallized on standing. GPC analysis showed that it consists of 96.9% unreacted 2,4,6-trimethylphenol, m.p. 66-68 °C. \( ^1\text{H}-\text{NMR (CCl}_4, \text{TMS, 25}^\circ\text{C): 2.15 ppm} \)
(s, 3H, p-Ar-CH₃), 2.16 ppm (s, 6H, o-Ar-(CH₃)₂), 4.20 ppm (s, 1H, Ar-OH),
6.63 ppm (s, 2H, Ar-H).

**Synthesis of PPO-OH by Phase Transfer Catalyzed Polymerization of 4-Bromo-2,6-dimethylphenol (20) in the Presence of (1)**

4-Bromo-2,6-dimethylphenol (20, 5.000 g, 24.9 mmol) and 1 (0.339 g, 2.49 mmol) were dissolved in 5 N aqueous NaOH (50 mL). Toluene (50 mL) and TBAH (0.422 g, 1.24 mmol) were added and the reaction mixture was vigorously stirred for 24 h at room temperature in the presence of air. The polymerization was quenched by neutralizing the reaction mixture with cold 1.5 N HCl. The toluene layer was separated and precipitated in methanol. The precipitate was filtered and dried in vacuo to yield 2.34 g (86%) of PPO-OH. $\overline{M}_n = 8,900$, $\overline{M}_w/\overline{M}_n = 1.62$.

**Synthesis of PPO-OH by Phase Transfer Catalyzed Polymerization of 20 in the Presence of 1′**

4-Bromo-2,6-dimethylphenol (20, 5.000 g, 24.9 mmol) and 1′ (0.443 g, 2.49 mmol) were dissolved in 1.5 N aqueous NaOH (50 mL). Benzene (50 mL) and TBAH (0.422 g, 1.24 mmol) were added. The reaction mixture was stirred for 24 h at room temperature in the presence of air. The polymerization was quenched by adding cold 1.5 N HCl until neutral. The benzene layer was separated and precipitated in methanol. The precipitate was filtered and dried in vacuo to yield 1.64 g (47.5%) PPO-OH. $\overline{M}_n = 6,100$; $\overline{M}_w/\overline{M}_n = 1.32$. 
Kinetic Experiments of the Phase Transfer Catalyzed Polymerization of 20 in the Presence of 1 or 1'

4-Bromo-2,6-dimethylphenol (20, 1.000 g, 4.97 mmol) and 1 (0.068 g, 0.50 mmol) or 1' (0.088 g, 0.50 mmol) were dissolved in 5 N aqueous NaOH (10 mL) or 1.5 N NaOH (10 mL), respectively. Benzene (10 mL) and TBAH (0.0844g, 0.25 mmol) were added. The reaction was stirred for a specific time at room temperature in the presence of air, and quenched by neutralizing with cold 1.5 N HCl. The benzene layer was separated and precipitated in methanol. The polymer was then filtered and dried in vacuo.

2.3. RESULTS AND DISCUSSION

2.3.1. Phase Transfer Catalyzed Homopolymerization of 2,4,6-Trimethylphenol (1)

The oxidation of 2,4,6-trimethylphenol (1) in the presence of water and excess of oxidant leads to PPO and 4,4'-dihydroxy-3,3',5,5'-tetramethyldiphenylmethane. The oxidative dealkylation mechanism suggested for their formation is shown in Scheme 2.1. The key intermediate of this mechanism is the phenoxy radical 6, formed by oxidation of 5. 4-Hydroxymethyl-2,6-dimethylphenol (5) is formed by oxidation of 1 to the quinone methide 4, followed by reaction of 4 with water (eq 1, Scheme 2.1). The phenoxy radical 6 can be attacked by either the phenoxy radical 2 (eq 2, Scheme 2.1) or the benzylic radical 2 (eq 3, Scheme 2.1) to give the unstable cyclohexadienone 7 and 9 intermediates. The cyclohexadienone 7 decomposes into 8 and formaldehyde, while 9 decomposes into 10 and formaldehyde. The phenoxy radical derived from oxidation of 8 can then react further, either with another phenoxy 8 radical or with 6, leading to
Scheme 2.1. Oxidative dealkylation of 2,4,6-trimethylphenol (1) in the presence of excess oxidant and water.
PPO-OH. Similarly, the oxidized 10 radical may react with 6 or with the oxidized 8 radical to generate PPO-2OH.\textsuperscript{3,4,7,9,12} 2,4,6-Trimethylphenol (1) is also reportedly dealkylated during oxidation with a copper-amine catalyst system.\textsuperscript{7,17} Requirements for the formation of the key intermediate 6 include a high concentration of oxidant, a two electron transfer oxidation process, the presence of water in the reaction mixture and the absence of reactants which consume the radical intermediates, 2 and 3. However, none of these reaction conditions occur under phase transfer catalyzed conditions. The concentration of oxidizable intermediates is determined by the concentration of the phase transfer catalyst present in the reaction mixture, and by the concentration of oxygen available in solution. Both are low. The radical intermediate 2 is consumed by other reactions and radical 2 does not exist in the reaction mixture. Therefore, generation of 4, 5, and subsequently 6 is not allowed. Under phase transfer catalyzed reaction conditions, 10 can not be generated because it requires the presence of both 6 and 3. However, the deprotonated form of 2 (14 in Scheme 2.2) can and does exist under these conditions.

Based on the above discussion, we assume that the oxidative dealkylation reactions of 2,4,6-trimethylphenol can not take place under phase transfer catalyzed reaction conditions. Nevertheless, in order to detect other possible side reactions occurring during the phase transfer catalyzed polymerization of 4-bromo-2,6-dimethylphenol in the presence of 2,4,6-trimethylphenol, we first attempted to homopolymerize 2,4,6-trimethylphenol. As expected, this homopolymerization reaction yields mainly unreacted 2,4,6-trimethylphenol. Therefore, after quenching and solvent removal, white crystals with melting point of 66-68°C grew from residue (pure 2,4,6-trimethylphenol, mp: 68-71°C). The 200 MHz \textsuperscript{1}H-NMR
spectrum of this residue is shown in Figure 2.1 (spectrum A). For the ease of peak assignments, the spectrum of the same sample after adding one drop of trichloroacetyl isocyanate into the NMR tube is presented as spectrum B in Figure 2.1. The corresponding spectra of pure 2,4,6-trimethylphenol both in the presence and absence of trichloroacetyl isocyanate are identical to those presented in Figure 2.1. The GPC trace of the product of the attempted polymerization is displayed in Figure 2.2, with unreacted 2,4,6-trimethylphenol representing 96.9% of the total residue. Therefore, only 3.1% of higher molecular weight oligomers were produced during the phase transfer catalyzed homopolymerization of 2,4,6-trimethylphenol.

Based on these results, we suggest that the alternative reaction mechanism presented in Scheme 2.2 takes place. In aqueous NaOH, 1 exists only as the corresponding phenolate 11, which is transferred into the organic phase as anonium phenolate upon addition of phase transfer catalyst. In the nonpolar aprotic solvent benzene, this onium phenolate 11 exists as an unsolvated ion-pair with reduced cation-anion interaction energy due to the bulky counter-cation. Therefore, it is more reactive than the corresponding sodium phenolate and is oxidized by oxygen from air to form the corresponding phenoxy radical 2 (eq 4, Scheme 2.2). Attack of the phenoxy radical 2 at the para position of phenolate 11 leads to 12 which can not decompose to 13 due to the strong C-CH3 bond (eq 5, Scheme 2.2). Therefore, 12 is a "radical sink".20 However, α-hydrogen abstraction reaction from either the para or ortho methyl groups of the phenolate anion 11 by the phenoxy radical 2 is favored by the electron donating character of the phenolate group (eq 6, Scheme 2.2). The radical anion 14 thus generated is a key intermediate in this polymerization. Because the reactivity of the radical 14 is lower than that of radical
Figure 2.1. 200 MHz $^1$H-NMR spectra (CCl$_4$, TMS, 25 °C) of the products resulted after evaporation of the benzene layer obtained from the phase transfer catalyzed polymerization of 2,4,6-trimethylphenol (1)(spectrum A); the $^1$H-NMR spectrum of the same sample after trichloroacetyl isocyanate was added into the NMR sample tube (spectrum B).
Figure 2.2. Gel permeation chromatography trace of the product resulted after the evaporation of benzene layer obtained from the phase transfer catalyzed polymerization of 2,4,6-trimethylphenol (I).
Scheme 2.2. The mechanism of the phase transfer catalyzed homopolymerization of 2,4,6-trimethylphenol (I).
3, 14 is less prone than 3 towards C-C coupling through its own benzyl radical.21 Also, since the phase transfer catalyzed reaction mixture does not contain free 1 but only its phenolate 11, direct oxidation of 1 to form 3 is excluded. However, generation of a benzyl radical by an intramolecular rearrangement has been previously observed during the oxidation of 4-methyl-2,6-di-tert-butylphenol21-25 and 2,4,6-trimethylphenol.21,23 This intramolecular rearrangement takes place through a 1,6 proton migration from the para methyl group to the phenoxy oxygen to form the phenol radical 2 (eq 7, Scheme 2.2).26 Although equation 7 is allowed, radical 3 does not exist under phase transfer catalyzed conditions since it is deprotonated to form 14 (eq 8, Scheme 2.2). Therefore, although radical 2 is more stable than 3, the latter generates the more stable radical anion 14. This shifts the equilibrium of equation 7 towards the right side. Because equations 6 and 7 minimize the availability of 2, 5 (eq 1, Scheme 2.1) is not formed under these reaction conditions.

The subsequent reactions of radical anion 14 determine what products result from the phase transfer catalyzed polymerization of 2,4,6-trimethylphenol. An energetically favorable reaction is the carbon-oxygen coupling between the phenoxy radical 2 and the radical anion 14 to form the benzyl ether dimeric anion 16 (eq 9, Scheme 2.2). The dimeric anion 16 can be oxidized to its phenoxy radical 17 (eq 10, Scheme 2.2). Radicals like 17 and 18 propagate by coupling with the radical anion 14 to form high molecular weight polymer. However, only a very low yield of oligomer (3.1%) results under these conditions, indicating that both the low reactivity of 17 and the low concentration of 14 are detrimental to polymerization. Also the initial propagation step shown in equation 9 (Scheme 2.2) involves the intermediates 2 and 14 which are present in very low concentrations. If the
polymerization would have involved the reaction of an intermediate such as 2 present in low concentration with a reactant present in high concentration (e.g., phenolate 11), high molecular weight polymers would be obtained in high yield.\textsuperscript{10,11} The present phase transfer catalyzed polymerization lacks a fast reaction step similar to equation 5 involving a co-reactant present in high concentration. Instead, the formation of polymer through equations 9, 10 and 11 consumes only a very small fraction of the phenolate 11 available in the reaction mixture.

Radical anion 14 may also dimerize to form the deprotonated 1,2-di(4-hydroxy-3,5-dimethylphenyl)ethane (19) (eq 12, Scheme 2.2). This reaction competes with the formation of 16 (eq 9) and 18 (eq 11). However, equations 9 and 11 are kinetically favored over equation 12. Therefore, the crosscoupling of 14 with 2 is favored over the dimerization of 14.

In conclusion, the only reasonable mechanism for the phase transfer catalyzed homopolymerization of 2,4,6-trimethylphenol is by the single electron transfer process outlined in Scheme 2.2. However, we have no direct structural evidence for the formation of a polybenzyl ether based on 17 and 18 due to the very low yield of polymer. Nevertheless, this structural evidence will be provided if benzyl ether structural units are incorporated in PPO-OH synthesized by the phase transfer catalyzed polymerization of 4-bromo-2,6-dimethylphenol in the presence of 2,4,6-trimethylphenol.

2.3.2. Phase Transfer Catalyzed Polymerization of 4-Bromo-2,6-dimethylphenol (20) in the Presence of 2,4,6-Trimethylphenol (1)

The phase transfer catalyzed polymerization of 4-bromo-2,6-dimethylphenol (20) was performed in the presence of various amounts of 2,4,6-trimethylphenol
(1). The results of these polymerization experiments are summarized in Table 2.1. Polymerizations performed with 20/1 molar ratios of 1/1 to 20/1 led to polymers with controllable molecular weight, monomodal molecular weight distribution (Figure 2.3), and polydispersities lower than 2.0. With higher molar ratios of 20/1 (i.e., 30/1 and 40/1) the resulting polymers display a bimodal molecular weight distribution (Figure 2.3, Table 2.1). Therefore, the polymerization of molar ratios of 20/1 of 1/1 to 20/1 is based on a single polymer homologous series, while those obtained from 20/1 molar ratios higher than 20/1 apparently contain two polymer homologous series which are obtained by two distinct propagation reactions.

The polydispersities and yields of methanol insoluble PPO-OH decrease with decreasing 20/1 molar ratio. This is due to the lower molecular weights involved and the resulting polymer fractionation by methanol precipitation. Figure 2.4 shows the GPC traces of different fractions of low molecular weight PPO-OH synthesized by polymerization with a 1/1 ratio of 20/1. Curve A is typical of the crude PPO-OH fraction obtained by solvent removal on a rotovapor. Curve B is typical of the methanol insoluble PPO-OH fraction which was separated by precipitating the toluene solution in methanol. Curve C corresponds to the methanol soluble PPO-OH fraction, obtained by evaporating the toluene/methanol filtrate after precipitation. Although the crude polymerization mixture has a broad polydispersity, methanol precipitation of PPO-OH with number average molecular weights below 9000 isolates less polymer, thereby resulting in lower yields of polymers that are more monodisperse.

With increasing PPO-OH molecular weight, solubility in methanol decreases, and most of the polymer sample is therefore separated by precipitation. The dependences of the number average molecular weight and the molecular weight
Table 2.1. Synthesis of PPO-OH by Phase Transfer Catalyzed Polymerization of 4-Bromo-2,6-Dimethylphenol (20) in the Presence of Various Amounts of 2,4,6-Trimethylphenol (1). Polymerization Solvent, Toluene/5N Aqueous NaOH; Polymerization Temperature, 25°C; Reaction Time, 24 h.

<table>
<thead>
<tr>
<th>Experiment No.</th>
<th>20/1 (mol/mol)</th>
<th>Polymer Yield (%)</th>
<th>$\bar{M}_n$ (g/mol)</th>
<th>$\bar{M}_w/\bar{M}_n$</th>
<th>Functionality of Chain End&lt;sup&gt;a&lt;/sup&gt;</th>
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<td>1.26</td>
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<td>55</td>
<td>6100</td>
<td>1.26</td>
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<td>95</td>
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<td>3.53</td>
<td>1.00</td>
</tr>
</tbody>
</table>

<sup>a</sup> Only 2,4,6-trimethylphenol chain end was observed on the 200 MHz $^1$H-NMR spectra.

<sup>b</sup> Bimodal molecular weight distribution.
Figure 2.3. Gel permeation chromatography traces of the PPO-OH synthesized from different initial molar ratios of 20/1: A) 20/1 = 1/1; B) 20/1 = 5/1; C) 20/1 = 30/1.
B: $\overline{M_n} = 4,400$
$\overline{M_w}/\overline{M_n} = 1.14$

Figure 2.4. Gel permeation chromatography tracce of different PPO-OH fractions synthesized with a 1/1 molar ratio of 20/1: A) raw PPO-OH obtained by evaporating the toluene solution; B) methanol insoluble PPO-OH fraction; C) methanol soluble PPO-OH fraction.
distribution are plotted as a function of the \(20/1\) molar ratio used in the initial reaction mixture in Figure 2.5. This figure demonstrates that the PPO-OH molecular weight can be controlled by polymerizing 4-bromo-2,6-dimethylphenol (20) in the presence of 2,4,6-trimethylphenol (1).

Figure 2.6 displays the 4 to 9 ppm region of several representative 200 MHz \(^1\)H-NMR spectra of PPO-OH synthesized with different \(20/1\) molar ratios. Spectrum A is of the PPO-OH synthesized using \(20/1 = 40/1\), while spectrum D is of the PPO-OH synthesized from 20 only. In spectrum D, only the 4-bromo-2,6-dimethylyphenoxy chain end (signal Z, 7.18 ppm), the 2,6-dimethylyphenylene ether structural units from the backbone (signal B, 6.38 ppm), and the 2,6-dimethylphenol chain end (signal E, 6.21 ppm) are observed. However, the resonance due to the 4-bromo-2,6-dimethylyphenoxy chain end at 7.18 ppm is absent in spectra of PPO-OH synthesized in the presence of 1 (spectra A, B, C in Figure 6). In addition to the expected 2,4,6-trimethylyphenoxy chain end (signal A, 6.80 ppm), 2,6-dimethylyphenylene ether structural units (signal B, 6.38 ppm), and 2,6-dimethylphenol chain end (signal E, 6.21 ppm), the spectra of PPO-OH synthesized in the presence of 1 exhibit other aromatic resonances (7.08, 6.94, 6.68 and 6.61 ppm) and resonances at 4.67, 4.59, and 4.56 ppm. Although 2,4,6-trimethylyphenoxy units are seen predominantly at the chain ends, these extraneous peaks are related to the internal 2,4,6-trimethylphenol derived structural units, and are not expected for a polymer in which 2,4,6-trimethylphenol functions as a chain initiator only.

The \(^1\)H-NMR spectra resulting from the addition of trichloroacetyl isocyanate to the samples presented in Figure 6 are shown in Figure 2.7. The 4.81 ppm resonance (spectrum C, Figure 6) is due to the OH proton of the 2,6-dimethyl-
Figure 2.5. The dependence of the number average molecular weight and the molecular weight distribution of the methanol insoluble fraction of PPO-OH on the 20/1 molar ratio in the initial reaction mixture (data from Table I).
Figure 2.6. 200 MHz $^1$H-NMR spectra of selected PPO-OH synthesized from 20 in the presence of 1 (expansion of 4 to 9 ppm, CCl$_4$, TMS, 25°C): A) 20/1 = 40/1; B) 20/1 = 10/1; C) 20/1 = 3/1; D) 20/1 = 1/0.
Figure 2.7. 200 MHz $^1$H-NMR spectra of the samples from Figure 6 after addition of trichloroacetyl isocyanate: A) $20/1 = 40/1$; B) $20/1 = 10/1$; C) $20/1 = 3/1$; D) $20/1 = 1/0$. 
phenol chain end since it is absent after adding the isocyanate, and a new -NH-
resonance appears at 8.32 ppm. The shoulder at 4.56 ppm (Spectrum C, Figure
2.6) is also sensitive to isocyanate, and is shifted downfield to 4.63 ppm (spectrum
C, Figure 2.7). This resonance must therefore be due to -OCH₂- (Q and R) protons
(Figures 2.6 and 2.7).

An expanded spectrum of the PPO-OH synthesized from 20/1=3/1 is
presented in Figure 2.8. This type of spectra is used to calculate the amount of
structural units derived from 2,4,6-trimethylphenol. The mol% of structural units
derived from 2,4,6-trimethylphenol incorporated as benzyl ether units (i.e., present
in the backbone as internal, penultimate and phenol chain end) are plotted as curve
A in Figure 2.9 as a function of the 20/1 molar ratio in the initial reaction mixture.
Curve A (Figure 2.9) demonstrates that the amount of 1 undergoing side reactions
decreases with increasing 20/1 ratios in the initial reaction mixture. The mol% of
benzyl ether units present as internal backbone units from the total benzyl ether units
is plotted as a function of the 20/1 ratio in Figure 2.9 (Curve B). Curve B indicates
that the amount of the internal backbone benzyl ether units derived from 1 increases
with increasing 20/1 molar ratio.

2.3.3. PTC Polymerization of 4-Bromo-2,6-Dimethylphenol (20) in
the Presence of 4-tert-Butyl-2,6-Dimethylphenol (1')

Because the side reactions which occur during the phase transfer catalyzed
polymerization of 20 in the presence of 1 are unavoidable, we have replaced 1 with
4-tert-butyl-2,6-dimethylphenol (1'), which can theoretically only be incorporated
as a PPO-OH chain end. The results of this polymerization are summarized in
Table 2.2. The range of controllable number average molecular weights extends
Figure 2.8. 200 MHz $^1$H-NMR spectrum of PPO-OH synthesized from $20/1 = 3/1$. An expansion of 4 to 9 ppm region with the assignments of the structural units derived from the side reactions (CCl₄, TMS).
Figure 2.9. The dependence of mol% benzyl ether units derived from 1 in the total structural units derived from 1 versus 20/1 molar ratio in the initial reaction mixture (curve A). The dependence of mol% of benzyl ether units present as internal backbone units from the total benzyl ether units versus 20/1 molar ratio in the initial reaction mixture (curve B).
Table 2.2. Synthesis of PPO-OH by Phase Transfer Catalyzed Polymerization of 4-Bromo-2,6-Dimethylphenol (20) in the Presence of Various Amounts of 4-tert-Butyl-2,6-Dimethylphenol (1'). Polymerization Solvent, Benzene/1.5N Aqueous NaOH; Polymerization Temperature, 25°C; Reaction Time, 24 h.

<table>
<thead>
<tr>
<th>Experiment No.</th>
<th>20/1' (mol/mol)</th>
<th>Polymer Yield (%)</th>
<th>$\overline{M}_n$ (g/mol)</th>
<th>$\overline{M}_w/\overline{M}_n$</th>
<th>Functionality of 1' Derived</th>
<th>Chain Enda</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>3</td>
<td>26</td>
<td>4600</td>
<td>1.40</td>
<td></td>
<td>1.00</td>
</tr>
<tr>
<td>2</td>
<td>5</td>
<td>34</td>
<td>5400</td>
<td>1.40</td>
<td></td>
<td>0.99</td>
</tr>
<tr>
<td>3</td>
<td>10</td>
<td>48</td>
<td>6100</td>
<td>1.32</td>
<td></td>
<td>0.97</td>
</tr>
<tr>
<td>4</td>
<td>20</td>
<td>59</td>
<td>7200</td>
<td>1.32</td>
<td></td>
<td>0.89</td>
</tr>
<tr>
<td>5</td>
<td>30</td>
<td>70</td>
<td>7900</td>
<td>1.30</td>
<td></td>
<td>0.85</td>
</tr>
<tr>
<td>6</td>
<td>40</td>
<td>74</td>
<td>9200</td>
<td>1.42</td>
<td></td>
<td>0.81</td>
</tr>
</tbody>
</table>

a) Determined by 200 MHz $^1$H-NMR spectroscopy.
from 4,600 to 9,200 with polydispersities from 1.32 to 1.42. The GPC traces of four representative PPO-OH's are presented in Figure 2.10. In contrast to the bimodal molecular weight distribution of PPO-OH prepared from 20/1 ratios of 30 and 40 (Figure 2.3), all polymerizations of 20 in the presence of 1' present monomodal molecular weight distributions. This indicates that the PPO-OH polymers synthesized with 1' as a co-reactant are formed by a single polymerization mechanism. Therefore, a single homologous series of PPO-OH are apparently derived from these polymerizations. Selected 200 MHz 1H-NMR spectra of these polymers are shown in Figure 2.11. PPO-OH polymers prepared from high 20/1' ratios (spectra A and B in Figure 2.11) exhibit two types of non-phenol chain ends, i.e. the 4-tert-butyl-2,6-dimethylphenoxy (signal A, 6.98 ppm) which accounts for 81 to 100% of the non-phenol chain ends, and a lower amount of 4-bromo-2,6-dimethylphenoxy chain ends (signal A', 7.18 ppm). Therefore, although two different types of chain initiators were present, the resulting polymers are homogeneous with respect to molecular weight and internal structural units, and appear to be a single homologous polymer series. This may be because the difference between the initiation and propagation rates of the two chains is not large enough to provide two different molecular weight distributions of the resulting PPO-OH polymers. The dependences of the number average molecular weight and of the functionality of the non-phenol chain end as a function of 20/1' ratio are plotted in Figure 2.12.

The PPO-OH synthesized from 20/1' = 10/1 was reacted with p-chloromethylstyrene as reported previously\textsuperscript{11} to obtain the corresponding vinylbenzyl ether (PPO-VBE). Its 200 MHz 1H-NMR spectrum is presented in Figure 2.13. As expected, the integral of the resonance of the four styrene aromatic
A: $\bar{M}_n = 5,400$, $\bar{M}_w/\bar{M}_n = 1.40$

B: $\bar{M}_n = 6,100$, $\bar{M}_w/\bar{M}_n = 1.32$

C: $\bar{M}_n = 7,200$, $\bar{M}_w/\bar{M}_n = 1.32$

D: $\bar{M}_n = 9,200$, $\bar{M}_w/\bar{M}_n = 1.42$

Figure 2.10. Gel permeation chromatography traces of the PPO-OH synthesized with different initial molar ratios of $20/1'$: A) $20/1' = 5/1$; B) $20/1' = 10/1$; C) $20/1' = 20/1$; D) $20/1' = 40/1$. 
Figure 2.11. 200 MHz $^1$H-NMR spectra of selected PPO-OH synthesized from 20 in the presence of 1' (expansion of 4 to 9 ppm, CCl$_4$, TMS, 25°C): A) 20/1' = 40/1; B) 20/1' = 20/1; C) 20/1' = 5/1.
Figure 2.12. The dependence of the number average molecular weight and the mol% concentration of 4-tert-butyl-2,6-dimethylphenoxycy chain end of PPO-OH on the $20/1'$ molar ratio used in the initial polymerization mixture (data from Table 2.2).
Figure 2.13. 200 MHz $^1$H-NMR spectrum of the $p$-vinylbenzyl ether derivative of PPO-OH synthesized with $20/1^1 = 10/1$ (CCl$_4$, TMS, 25°C).
protons (signal T, 7.32 ppm) is approximately two times that of the resonance from the 4-tert-butyl-2,6-dimethylphenoxy chain end (signal A, 6.98 ppm), demonstrating that the functionality for the non-phenol chain end listed in Table II (0.97) is correct. The other 3% must be due to 4-bromo-2,6-dimethylphenoxy chain ends. Therefore, the PPO-VBE macromonomer synthesized here has one vinylbenzyl ether unit per chain as desired, thus confirming that the PPO-OH synthesized from 20 in the presence of 1' contains only one phenol chain end.

2.3.4. Anion-Radical Mechanism of PTC Polymerizations

Based on these results, the mechanism of the phase transfer catalyzed polymerization of 20 in the presence of either 1 or 1' can be discussed. The mechanism of the phase transfer catalyzed homopolymerization of 20 is outlined in the left portion of Scheme 2.3. It was discussed previously\textsuperscript{10} by comparison with the non-phase transfer catalyzed process described by Price et al.\textsuperscript{27,28} The mechanism of the phase transfer catalyzed polymerization of 20 in the presence of 1 or 1' is outlined in the right portion of Scheme 2.3. Both mechanisms should be considered simultaneously since even in the presence of 1 or 1', the homopolymerization of 20 competes. Because 20 and 1 or 1' are first dissolved in aqueous NaOH, they are present in the reaction mixture as sodium 4-bromo-2,6-dimethylphenolate (21) and sodium 2,4,6-trimethylphenolate (11) or sodium 4-t-butyl-2,6-dimethylphenolate (11'). TBAH should transfer these anions into the organic phase with approximately equal probability since their lyophilicities are very similar. These phenolates are present in the nonpolar aprotic solvent (toluene or benzene) as nonsolvated ion-pairs with onium counter-cations and thus reduced cation-anion interaction. Therefore, they are much more reactive than the
Scheme 2.3. The mechanism of the phase transfer catalyzed polyetherification of 4-bromo-2,6-dimethylphenol (20) in the presence of 2,4,6-trimethylphenol (1) or 4-tert-butyl-2,6-dimethylphenol (1').
corresponding sodium phenolates and will be easily oxidized by oxygen from air to form the corresponding phenoxy radicals.

The experimental results presented so far suggest that the rate constant $k_3$ of oxidation of either the 2,4,6-trimethylphenolate (11) or 4-tert-butyl-2,6-dimethylphenolate (11') anions, is indeed larger than that of 4-bromo-2,6-dimethylphenolate (21), i.e. $k_1$. This is also due to the lower oxidation potentials of the phenolates containing electron donating groups in comparison to those containing electron withdrawing groups. However, the 4-bromo-2,6-dimethylphenoxy radical (22) is stabilized by resonance through the 4-bromo substituent, whereas both the 2,4,6-trimethylphenoxy radical (2) and 4-tert-butyl-2,6-dimethylphenoxy radical (2) are stabilized only by hyperconjugation of the $\alpha$-hydrogens. Because 22 is more stable than 2 or 2', 4-alkyl-2,6-dimethylphenoxy radicals 2 and 2' are more reactive than 22. Therefore, the rate constant $k_4$ of addition of the 2,4,6-trimethylphenoxy (2) or 4-tert-butyl-2,6-dimethylphenoxy (2') radicals to the 4-bromo-2,6-dimethylphenolate anion (21) is larger than the corresponding rate constant $k_2$ of addition of 4-bromo-2,6-dimethylphenoxy radical (22), i.e. $k_4 > k_2$. Based on similar reactivity considerations, $k_5 >> k_3 > k_1$ and $k_6 > k_4 > k_2$. The ratios between the rate constants $k_1$ versus $k_3$, and $k_2$ versus $k_4$ determine how controllable is the degree of polymerization of PPO-OH synthesized by phase transfer catalyzed polymerization of 20 in the presence of different amounts of 1 or 1'. The dependence of PPO-OH molecular weight on the 20/1 or 20/1' ratio is determined by the concentration of the 2,4,6-trimethylphenoxy radical (2) or of the 4-t-butyl-2,6-dimethylphenoxy radical (2) in the reaction mixture.

The polymerizations of $20/1 = 10/1$ and of $20/1' = 10/1$ were followed as a function of reaction time. The yields of both polymers are plotted in Figure 2.14 as
Figure 2.14. The dependence of the PPO-OH yield separated by precipitation in methanol on the polymerization time observed during the synthesis of PPO-OH: A) $20/1 = 10/1$; B) $20/1' = 10/1$. 

Methanol Insoluble PPO-OH Yield (%)

Polymerization Time (h)
a function of polymerization time. In both cases, the polymer yield increases with increasing the reaction time. The number average molecular weights of both PPO-OH polymers are plotted in Figure 2.15 as a function of polymerization time. By contrast to classic step polymerization reactions, the number average molecular weight of PPO-OH increases very rapidly at the beginning of polymerization. The $\bar{M}_n$'s of both PPO-OH polymers are plotted in Figure 2.16 as a function of polymer yield. The $\bar{M}_n$ is higher than expected for a step polymerization reaction since the reactivities of 28 and 28' are higher than those of 2, 2', and 22, i.e. $k_6 > k_4 > k_2$. Therefore, as previously discussed\textsuperscript{10} this polymerization reaction follows a "reactive intermediate polycondensation" kinetics\textsuperscript{4,10,12} which provides the molecular weight-yield pattern from Figure 2.16.

The present experimental results have shown that the PPO-OH polymers synthesized by the polymerization of various ratios of 20/1' contain 4-bromo-2,6-dimethylphenoxy chain ends in concentration ranging from 0 to 19% of the total non-phenol chain ends (Figure 2.12). This chain end is absent in PPO-OH synthesized from 20 in the presence of 1. This result can be explained by assuming that the rate determining step of polymerization is the generation of the phenoxy radicals by phenolate oxidation. If we consider only the electron donating effect of the phenolates' para substituents on their oxidizability, 11' must be more reactive than 11. However, as measured from the rate of oxygen consumption, the oxidation of the copper-amine complex of 1' is less than half that of 1.\textsuperscript{29} Therefore $k_3$ for 11' is smaller than $k_3$ for 11, and the ratio of $k_1/k_3$ is larger for 21/11' than for 21/11. This difference accounts for the presence of 0-19 % of 4-bromo-2,6-dimethylphenoxy chain ends in PPO-OH polymers obtained from 20/1' compared to the number of chain ends of this type in PPO-OH polymers prepared from 20/1.
Figure 2.15. The dependence of the number average molecular weight of PPPO-01 on the polymerization time: A) \(20/1 = 1/1\); B) \(20/1 = 0/1\).
Figure 2.16. The dependence of the number average molecular weight of PPO-OH on the yield of PPO-OH: A) $20/1 = 10/1$; B) $20/1' = 10/1$. 
During the phase transfer catalyzed polymerization of 20 in the presence of 1, α-H abstraction occurs, in a similar way to that described by equation 6 in Scheme 2.2. These reactions are presented in Scheme 2.4. In this case, hydrogen abstraction is caused by both the 2,4,6-trimethylphenoxy radical (2) (i.e. x = 0 in 32), and the 2,4,6-trimethylphenoxy terminated polymeric radical 32 (x > 1). This reaction may generate both radical anions 14 and 15 (equations 13 and 14, Scheme 2.4). Both radical anions can then participate in further propagation steps.

The resonance structures of the radical 2 and 32 are presented in Scheme 2.5. The difference in reactivity of the 2,4,6-trimethylphenoxy radical 2 and the polymeric radical 32 is very important in understanding the extent of side reactions taking place both during the polymerization of 20/1, and during the depolymerization of high molecular weight PPO-OH in the presence of 1. The depolymerization reaction is described in Chapter 5. The 2,4,6-trimethylphenoxy radical (2) is characterized by four resonance structures 2, 35, 36 and 37. The structures 35 to 37 are stabilized by hyperconjugation with the α-hydrogens to form delocalized radicals 38 to 40. This provides a total of nine α-H hyperconjugations available for the monomeric radical 2. The polymeric radical 32 has also four equivalent resonance structures: 32, 41, 42 and 43. Nevertheless, only 41 and 42 have α-hydrogens available for hyperconjugations represented by structures 44 and 45. The resonance form 43 can not resonate with structure 46 because oxygen's high electronegativity (3.5) decreases its ability to share its electrons with the benzene ring. Also, the highly unstabilized oxidized form of 1,4-benzoquinone 46 excludes structure 46 as a valid resonance form for the radical 43.

Both phenoxy radicals 2 and 32 are generated by the easy oxidation of the corresponding onium phenolates in the nonpolar aprotic polymerization solvent.
\[ \text{CH}_3\text{O}^- + R'\text{O}^- \rightarrow \overset{\text{eq 13}}{\text{HO}^-} + R'\text{OH} \]

\[ \text{CH}_3\text{O}^- + R'\text{O}^- \rightarrow \overset{\text{eq 14}}{\text{HO}^-} + R'\text{OH} \]

\[ R' = \text{CH}_3\left[\text{O}_{-}\right]_x, x = 0 \text{ to } n-1, \text{ where } n = \text{degree of polymerization} \]

Scheme 2.4. Hydrogen abstraction of 2,4,6-trimethylphenolate (11) under phase transfer catalyzed reaction conditions.
Scheme 2.5. Resonance stabilization of 2,4,6-trimethylphenoxy radical (2) and polymeric 4-aryloxy-2,6-dimethylphenoxy radical (32).
However, once formed, the polymeric radical 32 is less stable and therefore more reactive than the 2,4,6-trimethylphenoxy radical 2. In this case, the rate constant of hydrogen abstraction reactions induced by the polymeric phenoxy radical 32 (Scheme 2.4) are higher than the corresponding rate constant induced by the radical 2. Therefore, hydrogen abstraction (eqs 13 and 14, Scheme 2.4) should be more favored during the polymerization of 20 in the presence of 1 than during the homopolymerization of 1. This is shown to be true by the high amount of internal structural units derived from 1 (18-45% of the total structural units based on 1) (Figure 2.9). The amount of benzyl ether structural units based on 1 present in the polymer backbone decreases as the initial 20/1 ratio increases. Since the molar concentration of 20 was constant throughout these experiments, the molar concentration of the 2,4,6-trimethylphenolate (11) decreases with increasing 20/1 ratios. And because the concentration of reactant 11 determines the concentration of the phenoxy radical 2, the concentration of 2 decreases with increasing 20/1 ratio. The concentration of 32 and therefore of 14 also decrease with decreasing concentration of 1. As expected, the concentration of the benzyl ether internal structural units derived from 1 decreases with increasing 20/1 (Figure 2.9) since it is determined by the ratio of 20/1.

At this point, it is appropriate to discuss the relative ease of hydrogen abstraction from the ortho and para methyl groups of the phenolate 11. The resonance structures available for both radical anions 14 and 15 are outlined in Scheme 2.6. Even though 14 and 15 have equally stable delocalized resonance structures, the anion and radical in the primary radical anion 14 are separated by five bonds, whereas the radical and anion in 15 are separated only by three bonds. The more separated radical and anion in structure 14 makes it more stable than 15.
Scheme 2.6  Resonance structures of the para (14) and ortho (15) benzyl radical anions derived from 2,4,6-trimethylphenol (11).
Secondly, the *ortho* methyl groups in the 2,4,6-trimethylphenolate (11) are sterically hindered by the bulky tetrabutylammonium counter-cation. Therefore, the hydrogen abstraction at the *para* position to form 14 is favored over abstraction at the *ortho* position to form 15. However, the formation of 15 is stoichiometrically favored because 6 hydrogens are available for abstraction versus 3 hydrogens in the formation of 14. Therefore, we can not exclude the possible generation of a small amount of structure 15 during the polymerization of 20 in the presence of 1. Nevertheless, the radical anion 15 is probably less reactive towards C-O crosscoupling than is 14 due to higher steric hindrance. The absence of any side reaction products in the PPO-OH synthesized from 20 in the presence of 1' indicates that either the abstraction of hydrogen from the *ortho* methyl groups of 1', or the crosscoupling of 15' (similar to 15 but containing a 4-tert-butyl group instead of 4-methyl, Scheme 2.1) does not occur for steric reasons. That is, either side reaction may be prevented when a bulky t-butyl group is present in the para position instead of a methyl group.

The reactions involving the benzyl radical anions 14 and 15 in the phase transfer catalyzed polymerization of 20/1 are outlined in Scheme 2.7. The radical anion 14 first couples with the reactive polymeric radical 32 to form a benzyl ether linkage and the phenolate 53. Oxidation of the phenolate 53 leads to the 4-arylloxyethyl-2,6-dimethylphenoxy radical 54. Because 4-bromo-2,6-dimethylphenolate (21) is present in the reaction mixture in the highest concentration, the radical 54 preferentially reacts with it similarly to the normal propagation step discussed in Scheme 2.3. Elimination of Br- from the radical anion complex 55 gives a propagating polymeric phenoxy radical 56 containing a benzyl ether linkage in the polymer backbone. The new polymeric phenoxy radical 54 may
Scheme 2.7. Formation of benzyl-aryl ether units in the phase transfer catalyzed polymerization of 4-bromo-2,6-dimethylphenol (20) in the presence of 2,4,6-trimethylphenol (1).
also couple with another radical anion 14 or 15. Due to the low concentration of structures 54 and 14 or 15 if this reaction occurs, it gives a negligible concentration of 57. The corresponding reactions involving the ortho radical anion 15 are also outlined in the right portion of Scheme 2.7. Although generation of the para benzyl radical anion 14 is favored over generation of the ortho form 15 (Scheme 2.6), the present experimental results do not completely eliminate the participation of 15 in these reactions.

We should also compare the reactivities of the dimeric and oligomeric phenoxy radicals 28 (or 28') and 17 (or 17') respectively. The formation and reactions of these two radicals are represented in Scheme 2.8. The formation of the radical 28 (or 28') is kinetically favored over the formation of radical 17 (or 17') due to the higher concentration of phenolate 21 versus that of radical anion 14. Radical 28 (or 28') is less stable and therefore more reactive than radical 17 (or 17') due to the lower number of hydrogens available for resonance stabilization by hyperconjugation. Therefore, radical 28 (or 28') will propagate to the trimeric or oligomeric radical 62 (or 62') (eq 16, Scheme 2.8) faster than radical 17 (or 17') propagates to 63 (or 63') (eq 19, Scheme 2.8). The reactivities of 62 (or 62') and 63 (or 63') are identical. The rate constant of equation 16 is higher than that of equation 19. Therefore the polymer formed from growing dimeric or oligomeric species 28 (or 28') exhibits a higher molecular weight than that of the polymer formed from species 17 (or 17'). If the initial ratio of 20/1 in the reaction mixture is low, the concentration of 21 available to react with the radicals 2, 28 and 17 is also low. Consequently, the molecular weight of the PPO-OH derived from radical 28 (or 28') is higher than that of the polymer derived from 17 (or 17'). However, the difference between the molecular weights of these two polymers is small and is
Scheme 2.8. The structures and the propagation reactions of the two types of propagating radicals resulted during the phase transfer catalyzed polymerization of 4-bromo-2,6-dimethylphenol (20) in the presence of 2,4,6-trimethylphenol (1).
determined by the concentration of 21, which restricts the generation of high molecular weight polymers. Therefore, the PPO-OH obtained from low ratios of 20/1 does not display a bimodal molecular weight distribution. As the ratio of 20/1 increases, the concentration of phenolate monomer 21 available for the propagation of 28 and 17 also increases. In this case, both radicals 28 (or 28') and 17 (or 17') have sufficient phenolate monomer 21 to propagate to high molecular weight polymers since the concentration of 21 in the reaction mixture is high. The difference between the molecular weights of the polymers derived from these two growing species 28 (28') and 17 (17') increases with the 20/1 ratio. Therefore, as the 20/1 ratio increases to 30/1 and 40/1, the resulting PPO-OH polymers display a bimodal molecular weight distribution (Figure 2.3 and Table 2.1). The absence of bimodal molecular weight distributions for the polymers resulted from the homopolymerization of 20, 10, 11 and from the polymerizations of 20 in the presence of 1' further supports this reactivity explanation. In these last two cases, only one type of dimeric and oligomeric propagating radical similar in reactivity and structure to 28 (or 28') is formed.

Based on this polymerization mechanism, the most favored structures obtained by C-O crosscoupling which result during the phase transfer catalyzed polymerization of 20 in the presence of 1, are illustrated in Scheme 2.9. The 1H-NMR spectral assignments in Figure 2.8 are based on these structures. At the beginning of the polymerization, radical anion 14 derived from 2,4,6-trimethylphenol (Scheme 2.4) will react with 2,4,6-trimethylphenoxy radical 2 to result in the benzyl ether unit 16 (Scheme 2.8) which upon propagation generates the polymer 64 (Scheme 2.9). The 7.08 ppm resonance (Figure 2.8) is assigned to the aromatic protons (G in 64, Scheme 2.9) and the peak at 4.67 ppm is assigned to
Scheme 2.9. Structures of PPO-OH synthesized by the phase transfer catalyzed polymerization of 4-bromo-2,6-dimethylphenol (20) in the presence of 2,4,6-trimethylphenol (1).
the corresponding -OCH₂-protons (P in 64). A second benzyl ether penultimate
unit can be incorporated into PPO-OH like structure 65. The aromatic (H in 65) and
-OCH₂- (Q in 65) protons of this benzyl ether unit appear at 6.68 and 4.56 ppm,
respectively (Figure 2.8).

Structure 66 is produced by termination. The resonance at 6.61 ppm
(Figure 2.8) is assigned to the aromatic protons of the benzyl ether (I in 66, Scheme
2.9), while the -OCH₂- resonances of the same unit (R in 66) overlaps that of
corresponding penultimate unit (Q in 65) to give a shoulder at 4.56 ppm (Figure
2.8).

The highest concentration of benzyl-aryl ether structural units are internal
backbone units 67 (Scheme 2.9). The resonances at 6.94 and 4.59 ppm were
assigned to the aromatic (C in 67) and the -OCH₂- (O in 67) protons of the internal
benzyl ether units, respectively (Figure 2.8). The mol% of benzyl ether units
present as internal backbone units from the total benzyl ether units increases as
expected (Figure 2.9) with increasing the polymer molecular weight. This is due to
the fact that the probability of the benzyl ether groups located as penultimate (65)
and as the chain end (66) units (Scheme 2.9) decreases with increasing the polymer
molecular weight. The corresponding structures derived from the less favored
ortho radical anion 15 (Scheme 2.7) should form only in very low concentration
and their ¹H-NMR resonances probably overlap those of the para isomers. Scheme
2.9 therefore presents the benzyl ether structural units derived from the para isomers
only.

Although side reactions forming benzyl ether units occur during the
polymerization of 20 in the presence of 1, the PPO-OH derived from this phase
transfer catalyzed polymerization is monofunctional and contains only one 2,6-
dimethylphenol chain end. No bifunctional PPO-2OH can result from these polymerization reactions according to the reaction mechanism discussed.

2.4. CONCLUSIONS

The molecular weight of PPO-OH synthesized by the phase transfer catalyzed polymerization 4-bromo-2,6-dimethylphenol (20) in the presence of 2,4,6-trimethylphenol (1) can be controlled by the 20/1 molar ratio in the initial reaction mixture. The average molecular weight and polydispersity of the resulting PPO-OH increase with increasing 20/1 ratio. PPO-OH polymers of Mw/Mn between 1.14 to 1.26 have been obtained from 20/1 ratios ranging from 1 to 5. About 18-45% of the structural units derived from 1 have been incorporated into the polymer chain as benzyl ether units. These benzyl ether units are formed by α-hydrogen abstraction at the 4-methyl group of the 2,4,6-trimethylphenolate. The PPO-OH polymers synthesized from 20/1 ratios of 30 and 40 display a bimodal molecular weight distribution which results from two types of propagating dimeric and oligomeric species with different reactivities. The molecular weight of the PPO-OH polymers synthesized from 20 in the presence of 4-tert-butyl-2,6-dimethylphenol (1') can be controlled by the 20/1' molar ratio. The PPO-OH polymers obtained from 20/1' contain structural units derived from 1' present only as chain end and display a monomodal molecular weight distribution.
REFERENCES


CHAPTER 3

PTC POLYMERIZATION OF 4-BROMO-2,6-DIMETHYLPHENOL IN THE PRESENCE OF A BIFUNCTIONAL PHENOL

3.1. INTRODUCTION

The synthesis and characterization of \( \alpha, \omega \)-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 Brønsted 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 simultaneously developed.\(^3\)-\(^6\) In the one by Heitz et al.,\(^3\)-\(^5\) the molecular weight and the functionality of PPO-2OH are determined during the propagation step. In the technique by Nava and Percec,\(^6\) the molecular weight and the functionality of PPO-2OH were controlled by the redistribution reactions.
In Chapter 2, it was 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 lead perfectly monofunctional PPO-OH with controlled molecular weight. From the proposed anion-radical mechanism of polymerization, it should be possible to synthesize PPO-2OH by performing the PTC polymerization of BDMP in the presence of a bisphenol initiator. The first part of this chapter is to describe such a novel synthetic procedure for the synthesis of PPO-2OH oligomers. The particular example 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. The bifunctionality of the resulting PPO-OH was determined by $^1$H-NMR spectroscopy performed on PPO-2OH and on the $\alpha,\omega$-bis($p$-vinylbenzyl) ethers of PPO-2OH.

The second part of this chapter is concerned with the PTC reaction of 4-hydroxy-3,5-dimethylbenzyl alcohol (24) and the PTC polymerization of BDMP in the presence of 24. 24 was proposed as an intermediate from the oxidative dealkylation of 2,4,6-trimethylphenol when treated with excess manganese dioxide. Its formation requires a two-electron oxidation leading to a quinone methide, the experimental results from Chapter 2 suggest that 2,4,6-trimethylphenol does not generate this intermediate under PTC conditions. The investigation on the PTC reaction of pure 24 would therefore provide additional support for the previous proposed mechanisms. 24 is expected to be capable of controlling the molecular weight of PPO by PTC copolymerization of BDMP with 24, however, the hydroxymethyl group may undergo reactions under the PTC conditions.
Therefore, it is important to investigate both the structure and the functionality of the resulting copolymers.

3.2. EXPERIMENTAL

3.2.1. 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.

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(CH₃)₂-, 6H), 2.18 (s, Ph-CH₃, 12H), 4.47 (s, -Ph-OH, 2H), 6.82 (s, Ph-H, 4H).

Synthesis of 4-Hydroxy-3,5-dimethylbenzaldehyde

4-Hydroxy-3,5-dimethylbenzaldehyde was synthesized according to a literature procedure.\(^15\) Purity (HPLC): >99.9%. \(^1\)H-NMR: 2.31 (s, Ph-CH₃, 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°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%. ¹H-NMR: 2.25 (s, Ph-CH₃, 6H), 4.51 (s, Ph-CH₂OH), 4.62 (s, OH), 6.98 (s, 2 aromatic protons).

3.2.2. Polymerization Reactions

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)

The results of the polymerization experiments are listed in Table 3.1. 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 aqueous 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). $\bar{M}_n$ (GPC): 2700 g/mol, $\bar{M}_w/\bar{M}_n$=1.43.
Synthesis of $\alpha,\omega$-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. PPO-2OH (3, $M_n=3200$ g/mol, $M_w/M_n=1.41$, 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, 1.24 x $10^{-3}$ 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, 1.24X$10^{-4}$ mol) was added. The reaction mixture was stirred for 6 h at 25°C, and then acidified with excess 1.5 N aqueous 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. $M_n$ (GPC): 3900 g/mol, $M_w/M_n = 1.44$.

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°C in the presence of air for 24 h. The reaction was quenched by adding cold 1.5 N aqueous HCl. The benzene layer was separated, and benzene was removed on a rotovapor. The GPC and $^1$H-NMR analyses of the residue indicated that it contains 95% 4,4'-dihydroxy-3,3',5,5'-tetramethyl diphenyl methane 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

The results of the copolymerization experiments are summarized in Table 3.2. 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 °C in the presence of air for 24 h. The polymerization was quenched by neutralizing the reaction mixture with cold 1.5 N aqueous 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. $\bar{M}_n$ (GPC) = 20500, $\bar{M}_w/\bar{M}_n = 2.18$.

3. 3. RESULTS AND DISCUSSION

3.3.1. PTC Polymerization of 4-Bromo-2,6-dimethylphenol in the Presence of 2,2-Di(4-Hydroxy-3,5-dimethylphenyl)propane

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 3.1. The polymerization results are listed in Table 3.1. Polymerization experiments were performed with 1/2 molar ratios of 4/1, and by using either TBAH or Aliquat 336 as phase transfer catalysts. The obtained polymers have number average molecular weight ($\bar{M}_n$) in the range of 2200 to 3200 g/mol. 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

The structure of the PPO-2OH oligomers is determined by 200 MHz $^1$H-
Scheme 3.1. The phase transfer catalyzed synthesis of PPO-2OH and PPO-2VBE.
Table 3.1. 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).

<table>
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<th>Aliquat 336a</th>
<th>Yield (%), (GPC)</th>
<th>$M_n$ (g/mol)</th>
<th>$M_w/M_n$</th>
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<td>14</td>
<td>16</td>
<td>3000</td>
<td>1.41</td>
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</table>

a) tricaprylmethyl ammonium chloride.
NMR spectroscopy. For the polymerization performed for 12 h (Samples 2 and 5, Table 3.1), the polymer contains both 4-bromo-2,6-dimethylphenoxy\textsuperscript{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 3, Table 3.1) is shown in Figure 3.1. The protonic assignments are printed on the figure. A detailed discussion on their assignments was presented elsewhere.\textsuperscript{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)\textsuperscript{8,10} was observed in this $^1$H-NMR spectrum. The $M_n$ of the PPO-2OH can be determined from the integral ratio of resonances due to protons I + J to those due to K + L.\textsuperscript{6} The $M_n$ calculated from the $^1$H-NMR spectrum of sample No. 3 from Table 3.1 is 2300 g/mol, while the $M_n$ determined by GPC is 2600 g/mol.

In order to determine the chain end functionality of the PPO-2OH, the phenol chain ends were etherified under phase transfer catalyzed conditions with $p$-chloromethylstylene (eq 2, Scheme 3.1). A quantitative transformation of PPO-2OH into PPO-2VBE can be accomplished by this reaction.\textsuperscript{6,8,10} The 200 MHz $^1$H-NMR spectrum of the resulting PPO-2VBE is shown in Figure 3.2. 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 vinylbenzyl ether group is twice the integral of the L protons (4 protons each PPO-2OH molecule) in the 2
Figure 3.1. 200 MHz $^1$H-NMR spectrum (CDCl$_3$, TMS) of PPO-2OH (Sample No.3, Table 3.1).
Figure 3.2. 200 MHz $^1$H-NMR spectrum (CDCl$_3$, TMS) of PPO-2VBE (synthesized from Sample No. 3, Table 3.1) (an expansion of 4-8 ppm region).
derived unit. Therefore, the PPO-2OH synthesized by the phase transfer catalyzed copolymerization is indeed bifunctional.

Figure 3.3 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 3.1). 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.

Based on these experimental results, we propose the radical-anion mechanism of polymerization from Scheme 3.2. Equations 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 transferred into organic phase as the correspondingonium phenolates with tetrabutylammonium or tricaprylmethylammonium ions as their counter-cations. The first step of the polymerization is the oxidation of the phenolate group in the bisphenolate 6 to the corresponding phenoxy radical (eq 5). The phenoxy radical 7 then attacks the 4-position of the 4-bromo-2,6-dimethylphenolate (5) (eq 6) and the anion-radical intermediate 8 releases Br to form a dimeric phenoxy radical 9 (eq 7). The radical 9 subsequently repeats 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 the bis(phenoxy) radical 11 propagates leading to polymeric bisradicals 12 (eq 10). The termination of 10 yields polymer 13 which has a 2 derived terminal unit (eq 11). Figure 3.1 demonstrates the presence of this structural unit in small
Figure 3.3. GPC traces of PPO-2OH and PPO-2VBE: A) PPO-2OH (Sample No. 4, Table 3.1); B) PPO-2OH (Sample 3, Table 3.1); C) PPO-2VBE (synthesized from Sample 3, Table 3.1).
Scheme 3.2. The anion-radical 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 3.2 (Continued).
percentage. The termination of 12 produces the polymer structure 14 with 2 derived units located within the backbone (eq 12). Figure 3.1 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 (eqs 14, 15, and 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 3.1) the PPO-2OH polymers synthesized by a 24 h polymerization do not exhibit resonances due PPO-OH. Therefore, although PPO-OH could be initially formed, the subsequent redistribution reactions (eqs 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, they are lost during the purification process. Therefore, when this polymerization is performed for 24 h, it produces only bifunctional PPO-2OH.

3.3.2. PTC Polymerization of 4-Hydroxy-3,5-dimethylbenzyl Alcohol (24)

The phase transfer catalyzed homopolymerization of 4-hydroxy-3,5-dimethylbenzyl alcohol (24) did not yield a methanol insoluble fraction after 24 h of reaction. The benzene-methanol layer was therefore evaporated to a residue. The 200 MHz $^1$H-NMR spectrum of the residue is shown as Spectrum B in Figure 3.4. The corresponding $^1$H-NMR spectrum of 24 before reaction is shown as Spectrum
Figure 3.4. 200 MHz $^1$H-NMR spectra (CDCl$_3$, TMS) of 4-hydroxy-3,5-dimethylbenzyl alcohol (24) (Spectrum A) and the product of 24 after phase transfer catalyzed polymerization (Spectrum B).
A in Figure 3.4 for comparison. It is obvious that after reaction the aromatic resonance of 24 was shifted from 6.99 ppm to 6.78 ppm. The corresponding resonance due to CH2 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'-dihydoxy-3,3',5,5'-tetramethyldiphenylmethane and 5% oligomers. The PTC reaction of 24 is shown in eq 21 from Scheme 3.3.

A possible anion-radical mechanism for the PTC reaction of 4-hydroxy-3,5-dimethylbenzyl alcohol (24) is outlined in eq 22-36 from Scheme 3.3. Under PTC conditions, 24 is first deprotonated to form its phenolate 28 (eq 22). The phenolate 28 complexed with tetrabutylammonium cation is transferred into the benzene phase, where it is oxidized to its corresponding phenoxy radical 29 (eq 23). The elimination of OH⁻ from the phenolate 28 generates a anion-radical 30 (eq 24), similar to the quinone methide intermediate which was previously proposed in the oxidative polymerization of 2,4,6-trimethylphenol treated with excess manganese oxide.¹⁴ The benzyl radical in the anion-radical 30 attacks the phenolate 28 leading to the anion-radical intermediate 31 (eq 25). The elimination of formaldehyde¹⁴ yields the 4-hydro substituted radical-anion 32 (eq 26). 32 cannot enolize due to its phenolate anion structure. Therefore, the only reasonable elimination is assumed to take place by a radical hydrogen abstraction by the phenoxy radical 29 (eq 27). This reaction leads to the diphenylmethane diphenolate 33. The quenching of this reaction provides 2 protons to protonate the diphenolate 33 and leads to the neutral 4,4'-dihydroxy-3,3',5,5'-tetramethyldiphenylmethane (25) (eq 28). 25 accounts for 95% of this reaction products. As outlined in eqs 29 to 36 from Scheme 3.3 the rest of the products consists of 5% oligomers. The
Scheme 3.3. The proposed anion-radical mechanism for the phase transfer catalyzed polymerization of 4-hydroxy-3,5-dimethylbenzyl alcohol (24).
Scheme 3.3 (continued)
oxidation of the diphenolate 33 gives its corresponding phenoxy radical 34 (eq 29). 34 attacks the phenolate 28 (similar to eq 25) leading to the radical anion 35 (eq 30). 35 similarly eliminates formaldehyde (eq 31) and undergoes hydrogen abstraction (eq 32) forming the dimer phenolate 37. The repetition of eq 30-32 gives the trimer 38 (eq 33). This series of reactions leads to bifunctional oligomers. The other possible reactions that may lead to oligomers are shown in eq 34-36 from Scheme 3.3. These reactions start from the phenoxy radical 29, which attacks the phenolate 28 (eq 34), eliminating formaldehyde and undergoes hydrogen abstraction (eq 35) to give a monofunctional (referring to the phenol functionality) dimer 40. The repetition of reactions shown in eqs 34 and 35 gives the trimer 41 (eq 36) and oligomers.

The anion-radical mechanism (Scheme 3.3) was proposed based on the reaction pathway suggested for the formation of 25 from 24 during the oxidation of 2,4,6-trimethylphenol. An alternative mechanism for the formation of 25 which does not invoke the oxidation of 28 was suggested by Pearson. The mechanism consists of the nucleophilic addition of 28 to the para-quinone methide generated from 28 by elimination of OH-. The product resulting from the addition reaction was proposed to undergo the elimination of formaldehyde, however, this step was assumably assisted by OH-. This alternative mechanism is considered less probable under the present experimental conditions due to two unfavorable factors. The first factor is the low concentration of OH- in the benzene layer. This does not favor the OH- assisted formaldehyde elimination. The second factor refers to the role of oxidation step. It has been previously demonstrated that the formation of 25 from 24 requires oxidation.
<table>
<thead>
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<th>Exp. No.</th>
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<th>2</th>
<th>3</th>
<th>4</th>
</tr>
</thead>
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<td>2.18</td>
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</table>
Figure 3.5. 200 MHz $^1$H-NMR spectrum (CDCl$_3$, TMS) of a representative PPO polymer (Sample 1, Table 3.2).
3.3.3. PTC Polymerization of BDMP in the Presence of 4-Hydroxy-3,5-Dimethylbenzyl Alcohol

The phase transfer catalyzed copolymerization experiments of 4-bromo-2,6-dimethylphenol (1) with 4-hydroxy-3,5-dimethylbenzyl alcohol (24) are summarized in Table 3.2. These copolymerizations were performed with 1/24 molar ratio from 1/1 to 10/1, resulting in polymer yields from 71-95%. The number average molecular weights (Mn) of the polymers are in the range of 11100 to 27900 g/mol. The relative Mn as determined by GPC calibrated with polystyrene standards increase with increasing 1/24 molar ratio.

The 200 MHz ¹H-NMR spectrum of a representative PPO polymer (Sample 1, Table 3.2) is presented in Figure 3.5. 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 ppm downfield from the monomeric diphenylmethane (Spectrum B, Figure 3.4). 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 3.4). The Mn calculated from the ratio of the integrals of the resonance due to the backbone unit (Signal A, 6.47 ppm, Figure 3.5) to the resonances due to chain ends (6.94 ppm and 7.09 ppm) is 13000 g/mol. The ¹H-NMR spectrum indicates that the resulting PPO polymer represents a mixture of PPO-OH and PPO-2OH.

The 200 MHz ¹H-NMR spectrum of the p-vinylbenzyl ether derivative of the PPO polymer (Sample 1, Table 3.2) is presented in Figure 3.6. 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 3.6. 200 MHz $^1$H-NMR spectrum (CDCl$_3$, TMS) of the vinylbenzyl ether of the PPO polymer (Sample 1, Table 3.2).
Scheme 3.4. The proposed anion-radical mechanism for the phase transfer catalyzed copolymerization of 4-bromo-2,6-dimethylphenol (1) in the presence of 4-hydroxy-3,5-dimethylbenzyl alcohol (24).
Scheme 3.4 (Continued)
Based on the polymer structure determination, the PTC copolymerization reaction is shown in eq 37 from Scheme 3.4. To account for the polymer structure, a anion-radical mechanism for the polymerization is outlined in eq 38-50 from Scheme 3.4. The deprotonation of 4-bromo-2,6-dimethylphenol (1) is shown in eq 38 leading to its corresponding phenolate 5. The phenoxy radical 34 (eq 39) attacks the 4-bromophenolate 5 giving rise to an anion-radical 42 (eq 39). The subsequent bromide elimination from 42 produces a dimeric phenoxy radical 43 (eq 40). The repeated reactions (eqs 39 and 40) generate a polymeric phenoxy radical 44 (eq 41). The phenolate group in 44 can be oxidized to its phenoxy radical 45 (eq 42). The subsequent series of reactions of 45 (eqs 43-45) lead to a polymeric bisphenoxy radical 48. The termination of 48 generates the PPO-2OH 26 (eq 46). Similar anion-radical reactions of 4-hydroxymethyphenoxy radical 29 (generated by eq 23, Scheme 3.3) are shown in eqs 47-50 leading to PPO-OH with an \( \omega- \) (4-hydroxymethyl-2,6-dimethlphenoxy) group as the nonphenol chain end. The dependence of \( M_n \) on the molar ratio of 1/24 is determined by the relative concentrations of intermediates 34, 29, and 5 in a similar way as that previously discussed.8

3.4. CONCLUSIONS

The synthesis of perfectly bifunctional PPO-2OH has been 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 anion-radical mechanism.8,11-13
The phase transfer catalyzed (PTC) homopolymerization of 4-hydroxy-3,5-dimethylbenzyl alcohol (24) resulted in 95% 4,4'-dihydroxy-3,3',5,5'-tetramethyldiphenylymethane and 5% oligomers. The PTC polymerization of 4-bromo-2,6-dimethylphenol (1) in the presence of 24 led to a mixture of PPO-2OH and PPO-OH. Anion-radical mechanisms were proposed for these reactions.

REFERENCES

CHAPTER 4

PTC POLYMERIZATION OF 4-BROMO-2,6-DIMETHYLPHENOL IN THE PRESENCE OF A TERMINATING PHENOL

4.1. 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 proposed 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 an anion-radical 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 anion-radical 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

In Chapter 2, it was 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 anion-radical 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 (Chapter 3). The PTC polymerization of 4-bromo-2,6-dimethylphenol in the presence of 4-hydroxy-3,5-dimethylbenzyl alcohol was recently reported to yield a mixture of monofunctional (PPO-OH) and bifunctional (PPO-2OH) PPO (Chapter 3). However, there are no reported studies on the anion-radical polymerization of 4-bromo-2,6-dimethylphenol in the presence of a terminating phenol.

The first goal of this chapter 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 anion-radical mechanisms of these PTC polymerizations.

4.2. EXPERIMENTAL

4.2.1. 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.

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). ¹H-NMR: 1.42 (s, 18H, C(CH₃)₃), 5.00 (s, 1H, Ph-OH), 7.14 (s, 2H, 2 aromatic protons).

4.2.2. Polymerization Reactions

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

The results of the polymerization experiments are summarized in Table 4.1. 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 aqueous 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. \( \bar{M}_n \) (GPC) = 13400, \( \bar{M}_w/\bar{M}_n = 2.96. \)
4.3. RESULTS AND DISCUSSION

4.3.1. PTC Polymerization of BDMP in the Presence of 2,4,6-Tri-tert-butylphenol.

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 eqs 1 to 3 from Scheme 4.1. The polymerization results are listed in Table 4.1.

For the polymerization of bromo-2,6-dimethylphenol (1) in the presence of 2,4,6-tri-tert-butylphenol (2) (eq 1, Scheme 4.1), a 1/2 molar ratio of 3/1 resulted in a PPO with $M_n = 13400$ and $M_w/M_n = 2.96$ (Experiment 1, Table 4.1).

The 200 MHz $^1$H-NMR spectrum of the resulting PPO polymer (Sample No. 1, Table 4.1) is shown in Figure 4.1. 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 ($M_n$) 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.

The anion-radical mechanism suggested for the phase transfer catalyzed polymerization of 1 in the presence of 2 is outlined in eqs 4-14 from Scheme 4.2. Because 2,4,6-tri-tert-butylphenol (2) is only soluble in organic phase,\textsuperscript{21} it is deprotonated in the organic phase by either 4-bromo-2,6-dimethylphenolate (9) or OH\textsuperscript{-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,\textsuperscript{23,24} with nitrogen dioxide radical,\textsuperscript{25} and with neutral molecules such as acetic acid and methanol.\textsuperscript{26}
Scheme 4.1. Phase transfer catalyzed polymerizations of 1 in the presence of 4-substituted-2,6-di-tert-butylphenol (2 and 4).
Table 4.1. 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.

<table>
<thead>
<tr>
<th>Exp. No.</th>
<th>1 (mmol)</th>
<th>Comonomer/ (mmol)</th>
<th>1/Comonomer (mol/mol)</th>
<th>Polymer Yield (%)</th>
<th>Mn (GPC) (g/mol)</th>
<th>Mw/Mn</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>9.96</td>
<td>2/3.31</td>
<td>3/1</td>
<td>85</td>
<td>13400</td>
<td>2.96</td>
</tr>
<tr>
<td>2</td>
<td>4.98</td>
<td>4/1.00</td>
<td>5/1</td>
<td>0⁴</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>3</td>
<td>4.98</td>
<td>4/0.50</td>
<td>10/1</td>
<td>0⁴</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>4</td>
<td>9.96</td>
<td>4/1.00</td>
<td>10/1</td>
<td>0⁴</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>5</td>
<td>9.96</td>
<td>4/1.00b</td>
<td>10/1</td>
<td>26</td>
<td>1600</td>
<td>2.10</td>
</tr>
<tr>
<td>6</td>
<td>9.96</td>
<td>4/1.00c</td>
<td>10/1</td>
<td>42</td>
<td>2400</td>
<td>1.66</td>
</tr>
</tbody>
</table>

a) No methanol insoluble polymer was obtained, i.e. no PPO polymer with Mn>800 g/mol⁸ 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.
Figure 4.1. 200 MHz $^1$H-NMR spectrum (CDCl$_3$, TMS) of polymer (Sample No. 1, Table 4.1).
The radical 7 has been used as an initiator for the non-phase transfer catalyzed polymerization of 4-bromo-2,6-dimethylphenol,\textsuperscript{21} 4-bromo-2,6-disubstituted phenols,\textsuperscript{27} and for the redistribution reactions of phenol dimers.\textsuperscript{28} Radical 7 initiates the polymerizations by proton abstraction from the monomers' phenolic OH.\textsuperscript{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-\textit{tert}-butylphenoxo radical (7) on the 2,4,6-tri-\textit{tert}-butylphenolate (6) (eq 6) does not occur due to steric hindrance both at the phenoxy radical site in 7 (caused by two bulky \textit{tert}-butyl groups at the \textit{ortho} positions) and at the 4-position in 6 by the 4-\textit{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 an anion-radical reaction takes place by the attack of the phenoxy radical 10 on the phenolate 9 (eq 9). This attack leads to the anion-radical intermediate 11 (eq 9). The bromide elimination from 11 yields the dimer phenoxy radical 12 (eq 10). The repeated reactions shown in eqs 9 and 10 produce the polymeric phenoxy radical 13 (eq 11). The attack of 2,4,6-tri-\textit{tert}-butylphenoxo 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-\textit{tert}-butylphenol (2) derived species is a anion-radical reaction of a growing polymeric phenoxy radical 13 at the 4-position of the 2,4,6-tri-\textit{tert}-butylphenolate (6) (eq 13), leading to 4-\textit{tert}-butyl anion-radical 15. Due to the steric hindrance by the bulky 4-\textit{tert}-butyl group this reaction is not kinetically favored and therefore, 15 dissociates back to the starting radical and anion. 15 is also incapable of eliminating 4-\textit{tert}-butyl group in a
Scheme 4.2. The mechanism proposed for 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 4.2 (Continued)
similar way 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 $M_n$ 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.

4.3.2. PTC Polymerization of BDMP in the Presence of 4-Bromo-
2,6-Di-tert-Butylphenol (4)

The polymerization of 1 in the presence of 4 is presented in eq 2 and 3 from
Scheme 4.1. 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 4.1). These
polymerization experiments failed to produce any methanol insoluble PPO (usually
$M_n > 800$ g/mol) (Exp. No. 2-4, Table 4.1). 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 4.1)
is shown in Figure 4.2. From the resonances of high intensity at 2.21 and 7.10
ppm and the GPC 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
Figure 4.2. 200 MHz $^1$H-NMR spectrum (CDCl$_3$, TMS) of the residue after evaporation of benzene from the organic layer (Exp. No. 2, Table 4.1).
the 2,6-dimethylphenoxy repeating unit of PPO (cf. the assignment structure in Figure 4.2) 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 ($\bar{M}_n < 800$ g/mol). Figure 4.2 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 4.1). PPO in 24 to 42% yields were obtained with $\bar{M}_n$ from 1600 to 2400 g/mol from these two experiments (Exp. No. 5 and 6, Table 4.1). The 200 MHz $^1$H-NMR spectrum of a typical PPO polymer prepared by this method (Exp. No. 6, Table 4.1) is presented in Figure 4.3. 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 4.2) 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.

The mechanism for the polymerization of 1 in the presence of 4 is presented in eqs 15-22 from Scheme 4.2. The deprotonation of 4 and the subsequent oxidation of the phenolate 17 are shown in eqs 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
Figure 4.3: 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).
its 4-position yielding the anion-radical 21. However, for anion-radical 21 the bromide elimination represents a favorable reaction (similar to eq 10) which produces a 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 4.1) produced only some oligomers (Figure 4.2) 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). There are two possible reasons 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). Therefore, eq 19 is more favored than eq 13. Secondly, the anion-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 stable radical 22 which is incapable of propagation. In contrast, the anion-radical 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.
4.4. 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 of propagation. 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 ($\bar{M}_n = 1600 - 2400$ g/mol) was obtained when 4 was added a short period after the homopolymerization of 1 was started.
REFERENCES


CHAPTER 5

PHASE TRANSFER CATALYZED DEPOLYMERIZATION
OF PPO-OH IN THE PRESENCE OF EITHER 2,4,6-
TRIMETHYLPHENOL OR 4-tert-BUTYL-2,6-
DIMETHYLPHENOL

5.1. INTRODUCTION

It seems to be generally accepted that the synthesis of poly(2,6-dimethyl-
1,4-phenylene oxide) (PPO) can be performed by two different reaction
mechanisms. The first mechanism is based on the addition of an aryloxy radical
to an aryloxy radical. It is considered to be responsible for the oxidative
polymerization of 2,6-dimethylphenol. 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.

Recently, a phase transfer catalyzed procedure for the polymerization of 4-
bromo-2,6-dimethylphenol has been developed. 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 Chapter 2.

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 and it is considered that it
stops before the thermodynamic equilibrium is reached.\textsuperscript{12,15} However, to our knowledge, there is no report in the literature on the depolymerization of PPO by a anion-radical mechanism.

The first goal of this chapter is to describe the phase transfer catalyzed depolymerization of PPO-OH in the presence of either 2,4,6-trimethylphenol or 4-\textit{tert}-butyl-2,6-dimethylphenol. The second goal of this chapter is to discuss the anion-radical PTC depolymerization mechanism.

\section*{5.2. EXPERIMENTAL}

\subsection*{5.2.1. Materials}
Poly(2,6-dimethyl-1,4-phenylene oxide) (I, \textit{PPO}, $\overline{M}_n = 20,000$, $M_w/M_n = 3.08$) with bimodal molecular weight distribution was obtained from Aldrich. PPO-OH (I, $\overline{M}_n = 17,800$, $M_w/M_n = 1.39$) with monomodal molecular weight distribution and the vinyl benzyl ether of I (PPO-VBE, $\overline{M}_n=26,600$, $M_w/M_n=1.22$) were synthesized as reported previously.\textsuperscript{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-\textit{tert}-Butyl-2,6-dimethylphenol (2') was synthesized as described in a previous publication.\textsuperscript{11}

\subsection*{5.2.2. PTC Depolymerization Reactions}

\textbf{Phase Transfer Catalyzed Depolymerization of Bimodal PPO (1) in the Presence of Either 2,4,6-Trimethylphenol (2) or 4-\textit{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 (1.00 g, 0.05 mmol) in 20 mL benzene was added a solution of 2 (0.50 g, 3.67 mmol) in 20 mL of 1.5N aqueous NaOH, followed by 0.169 g (0.5 mmol) of TBAH. The reaction mixture was stirred for 24 h at room temperature in the presence of air, after which it was quenched by neutralizing with cold 1.5 N aqueous HCl. The benzene layer was separated and precipitated in methanol. The precipitate was filtered and dried \textit{in vacuo} to yield 0.53 g (53\%) PPO-OH. $\bar{M}_n = 5,700$, $\bar{M}_w/\bar{M}_n = 5.79$.

**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, 4.00 g, 0.20 mmol) was dissolved in benzene (80 mL). A solution of 2 (0.80 g, 5.88 mmol) dissolved in 40 mL of 1.5N NaOH and 0.103 g (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 aqueous HCl. The benzene layer was separated, precipitated in methanol and the precipitate was filtered and dried \textit{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, 2.00 g, 0.112 mmol) was dissolved in a mixture of 12 mL benzene and 12 mL THF. A solution of 2 (0.20 g, 1.5 mmol) in 12 mL of 1.5N aqueous NaOH and 0.224 g (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 (0.237 g, 0.0089 mmol) was dissolved in 5 mL benzene. A solution of 2' (0.05 g, 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 h at room temperature in the presence of air. The reaction was then quenched by neutralizing with cold 1.5 N aqueous HCl. The benzene layer was separated and precipitated in methanol to yield 0.208 g (87%) PPO-VBE.

5.3. RESULTS AND DISCUSSION

5.3.1. PTC Depolymerization Reactions

The depolymerization reaction of PPO (1) in the presence of 2,4,6-trimethylphenol (2) or 4-tert-butyl-2,6-dimethylphenol (2') is represented in Scheme 5.1. 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 5.1. 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 5.1. 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
Scheme 5.1. 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').

\[
\begin{align*}
\text{X} & \quad \text{O} \quad \begin{array}{c} \text{O} \end{array} \quad \text{O} \quad \begin{array}{c} \text{OH} \end{array} + R \quad \begin{array}{c} \text{O} \end{array} \quad \text{OH} \\
\text{X} = \text{H, Br} \\
1 & \\
2, R = \text{CH}_3 \\
2', R = \text{C(CH}_3)_3 \\
3 & \\
n' < n \\
\text{Benzen}/1.5 \ N \ NaOH (aq) & \quad \text{TBAH} \\
\text{4(4')} & \\
n'' > 1
\end{align*}
\]
Table 5.1. Synthesis of PPO-OH by Phase Transfer Catalyzed Depolymerization of PPO (1, $\bar{M}_n = 20,000$; $\bar{M}_w/\bar{M}_n = 3.08$) in the Presence of Various Amounts of 2,4,6-Trimethylphenol (2). (Depolymerization solvents, benzene and 1.5 N aqueous NaOH; depolymerization temperature, 25°C; reaction time, 24 h; phase transfer catalyst, TBAH).

<table>
<thead>
<tr>
<th>Experiment No.</th>
<th>$\frac{1/2}{(wt/wt)}$</th>
<th>$\frac{1/2}{(mol/mol)}$</th>
<th>Yield (%)</th>
<th>$\bar{M}_n$ (GPC)</th>
<th>$\bar{M}_w/\bar{M}_n$ (GPC)</th>
<th>Undepolymerized PPO (% area)</th>
<th>Depolymerized PPO (peak $\bar{M}_w/%$ area)</th>
</tr>
</thead>
<tbody>
<tr>
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<td>1/1</td>
<td>0.0068/1</td>
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<td>20,600</td>
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<td>-</td>
</tr>
<tr>
<td>2</td>
<td>2/1</td>
<td>0.0136/1</td>
<td>53</td>
<td>5,700</td>
<td>5.79</td>
<td>31</td>
<td>6,700/69</td>
</tr>
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<td>3</td>
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<td>4.82</td>
<td>16</td>
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</tr>
<tr>
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<td>0.068/1</td>
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<td>5,300</td>
<td>3.47</td>
<td>-</td>
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</tr>
<tr>
<td>5</td>
<td>16.7/1</td>
<td>0.114/1</td>
<td>86</td>
<td>6,900</td>
<td>3.61</td>
<td>-</td>
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<tr>
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<td>0.340/1</td>
<td>87</td>
<td>9,000</td>
<td>3.57</td>
<td>-</td>
<td>14,800/-</td>
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Figure 5.1. GPC traces of PPO resulted from resulted from different initial $1/2$ molar ratios.
weight of this peak are listed in Table 5.1. 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 5.1, Figure 5.1). 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.

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. 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 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.

A second series of depolymerization experiments of the bimodal PPO were performed in the presence of 2'. The corresponding results are presented in Table 5.2. The GPC traces from Figure 5.2 demonstrate the dependence of the final
Table 5.2. Synthesis of PPO-OH by Phase Transfer Catalyzed Depolymerization of PPO (1, $M_n = 20,000$; $M_w/M_n = 3.08$) in the Presence of Various Amounts of 4-tert-Butyl-2,6-Dimethylphenol (2). (Depolymerization solvents, benzene and 1.5 N aqueous NaOH; depolymerization temperature, 25°C; reaction time, 24 h; phase transfer catalyst, TBAH).

<table>
<thead>
<tr>
<th>Experiment No.</th>
<th>$1/2'$ (wt/wt)</th>
<th>$1/2'$ (mol/mol)</th>
<th>Yield (%)</th>
<th>$M_n$ (GPC)</th>
<th>$M_w/M_n$ (GPC)</th>
<th>Undepolymerized PPO (% area)</th>
<th>Depolymerized PPO (peak $M_w$/% area)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>1/1</td>
<td>0.0089/1</td>
<td>39</td>
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<td>6.91</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
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<td>2/1</td>
<td>0.0178/1</td>
<td>52</td>
<td>4,400</td>
<td>6.88</td>
<td>33</td>
<td>4,800/67</td>
</tr>
<tr>
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<td>5/1</td>
<td>0.0445/1</td>
<td>73</td>
<td>5,000</td>
<td>4.08</td>
<td>13</td>
<td>7,600/87</td>
</tr>
<tr>
<td>4</td>
<td>10/1</td>
<td>0.089/1</td>
<td>86</td>
<td>7,100</td>
<td>4.06</td>
<td>-</td>
<td>9,500/-</td>
</tr>
<tr>
<td>5</td>
<td>16.7/1</td>
<td>0.149/1</td>
<td>87</td>
<td>7,600</td>
<td>3.59</td>
<td>-</td>
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<td>0.445/1</td>
<td>90</td>
<td>12,500</td>
<td>3.38</td>
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Figure 5.2. GPC traces of PPO resulted from different initial $1/2'$ molar ratios.
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.

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 5.3. The resonance due to the 2,4,6-trimethylphenoxoxy 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. The NMR spectra of the PPO-OH resulted from the depolymerization of 1 in the presence of 2' are presented in Figure 5.4. All these spectra present the resonance at 6.98 ppm which is due to the 4-tert-butyl-2,6-dimethylphenoxoxy chain end.

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 5.5. 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 5.6.

A sample of monomodal PPO-OH with $\bar{M}_n = 17,800$ and $\bar{M}_w/\bar{M}_n = 1.39$ was depolymerized in the presence of 2 at an initial ratio $1/2$=0.068/1. The GPC
Figure 5.3. 200 MHz $^1$H-NMR spectra of PPO resulted from different initial $1/2$ molar ratios.
Figure 5.4. 200 MHz $^1$H-NMR spectra of PPO resulted from different initial $1/2'$ molar ratios.
Figure 5.5. GPC traces of PPO resulted from bimodal \( \downarrow \) at different reaction times (\( 1/2 = 0.034/1 \)).
Figure 5.6. Dependence of % depolymerized PPO on reaction time ($1/2=0.034/1$).
traces of the methanol insoluble PPO-OH obtained at several different reaction times are presented in Figure 5.7. After 24 h of depolymerization time the newly formed PPO-OH represents 91.6% of the entire polymer sample (trace D in Figure 5.7). The amount of PPO-OH formed during this depolymerization is plotted as a function of the reaction time in Figure 5.8. 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 5.9. The amount of PPO-OH formed by depolymerization of a $1/2'$ ratio of 0.089/1 is plotted in Figure 5.10 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 $^1$H-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.

The depolymerization experiments 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, the polymers obtained by depolymerization display a bimodal
Figure 5.7. GPC traces of PPO-OH resulted from monomodal 1 in the presence of 2 at different reaction times (1/2=0.068/1).
Figure 5.8. Dependence of % depolymerized 1 on reaction time (monomodal 1 in the presence of 2.)
Figure 5.9. GPC traces of PPO-OH resulted room monomodal 1 in the presence of 2 at different reaction times (1/2=0.089/1).
Figure 5.10. Dependence of % depolymerized \( \mathbf{1} \) on the reaction time (monomodal \( \mathbf{1} \) in the presence of \( \mathbf{2} \)).
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 benzylc 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 benzylc structural units.

5.3.2. Anion-Radical Mechanism for the PTC Depolymerization

The deprotonation mechanism of the PPO-OH is presented in Scheme 5.2. 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 5.2. 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 5.¹⁷, ¹⁸ The second possible deprotonation reaction is presented in equation 3 from Scheme 5.2. It consists of the deprotonation of PPO-OH 1, by the tetrabutylammonium phenolate 7. Due to the high lipophilicity of this organiconium phenolate, equation 3 is kinetically more favored than equation 2. The resonance structures of the monomeric phenolate 7 are shown as structures 7, 2, 10, and 11 (equation 4, Scheme 5.2). The corresponding four resonance structures of the polymeric phenolate 8 i.e., 8, 12, 13, and 14 are shown in equation 5 from Scheme 5.2. Structure 15 is not a valid resonance structure under the PTC anion-radical reaction conditions.¹⁹ The phenolate 7 has an electron-donating group which increases the electron density.
Scheme 5.2. The deprotonation mechanism of PPO-OH (1) during the phase transfer catalyzed depolymerizations.
of the phenylene ring. This makes the monomeric phenolate 2 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 5.1). Therefore, eq 3 from Scheme 5.2 represents the thermodynamically favored deprotonation reaction.

Even though two mechanisms are possible for the deprotonation of high molecular weight PPO-OH (eqs 2 and 3, Scheme 5.2), the overall deprotonation process is very slow. The experimental results presented in Figures 5.5, 5.7 and 5.9 provide several observations. First, the deprotonation is slow as indicated by the time required for any observable depolymerization. Therefore, the induction period is usually several hours. Secondly, the residual high molecular weight PPO-OH does not decrease its molecular weight as the depolymerization proceeds. This indicates that only a fraction of PPO-OH is deprotonated and is therefore capable of depolymerizing during the depolymerization experiments. At the end of the depolymerization experiments, there is still a PPO-OH fraction which has the initial molecular weight. This suggests that the deprotonation is not 100%. All these effects suggest that the equilibrium constants for both eqs 2 and 3 are lower than those required by the complete deprotonation. The decrease in the amount of the undepolymerized PPO-OH with the reaction time implies that the PPO-OH is gradually deprotonated. The fact that the amount of depolymerized fraction reaches an equilibrium is most probably caused by the gradual decrease of the phenolate concentration and by the subsequent decrease in the rate of reinitiation.

The depolymerization mechanism of the phase transfer catalyzed process is presented in Scheme 5.3. Equation 6 shows the generation of the phenoxy radical through the oxidation of the corresponding phenolate 5 by air-oxygen. This process was discussed in detail previously. The oxidation of polymer phenolate
Scheme 5.3. Anion-radical mechanism of the phase transfer catalyzed depolymerization.
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. 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 5.3). 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.
Scheme 5.4. Possible side reactions of 2,4,6-trimethylphenol (2).
In conclusion, the redistribution reaction of the phase transfer catalyzed depolymerization proceeds according to a anion-radical mechanism as shown in equation 8 from Scheme 5.3.

The depolymerization through equation 8 (Scheme 5.3) results in PPO-OH with either 2,4,6-trimethylphenoxy or 4-tert-butyl-2,6-dimethylphenoxy chain ends. This reaction generates two polymer molecular weight 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 $16$.\textsuperscript{20}

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 5.4. This side reaction consists of the $\alpha$-hydrogen abstraction from the phenolate $5$ by a polymeric radical $17$ and leads to the anion-radical $30$. The intermediate $30$, if generated at all, will participate in the polymerization reaction (equation 14, Scheme 5.4) leading to a polymeric radical containing benzyl ether units. As shown in Section 5.3.1,\textsuperscript{20} 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 5.4). 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 5.3. 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.\textsuperscript{11} Therefore, equation 15 is less favored than equation 16. This makes the participation of 33 in the 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.

5.4. CONCLUSIONS

The PTC depolymerization of high molecular weight PPO-OH in the presence either 2,4,6-trimethylphenol or 4-tert-butyl-2,6-dimethylphenol yields PPO-OH of similar structure as the PPO-OH resulted from the PTC polymerization of 4-bromo-2,6-dimethylphenol. The PPO-OH obtained from the depolymerization has a bimodal molecular weight distribution, which represents the PPO-OH growing from the initiating phenol and the high molecular weight PPO-OH after depolymerization. The PTC depolymerization proceeds by an anion-radical mechanism in which the phenoxy radical derived from the initiating phenol attacks the terminal unit of a polymeric phenolate.

REFERENCES


PART II
SYNTHESIS OF AROMATIC POLYETHERS
BY CATION-RADICAL REACTIONS
CHAPTER 6

ON THE POLYMERIZABILITY OF 4,4'-BIS(PHENOXY)SULFONES AND OF 4,4'-BIS(PHENYLTHIO)DIPHENYL SULFONE IN THE CATION-RADICAL POLYMERIZATION REACTIONS

6.1 INTRODUCTION

Aromatic polyether sulfones and polyether ketones are frequently synthesized by variants of aromatic nucleophilic substitution and aromatic electrophilic sulfonylation or acylation reactions.\textsuperscript{1-8} Two novel approaches to the synthesis of both polyethersulfones and polyetherketones were recently reported. The first one consists of the Scholl reaction of 4,4'-di(1-naphthoxy)diphenyl sulfone and of 4,4'-di(1-naphthoxy)benzophenone, which leads to poly(4,4'-dinaphthyl ether phenyl sulfone)s and poly(4,4'-dinaphthyl ether phenyl ketone)s.\textsuperscript{9} The formation of the C-C aromatic bonds during this polymerization process is assumed to occur through a radical-cation mechanism. The second method consists of a Ni\textsuperscript{0} catalyzed crosscoupling of 4,4'-di(p-chlorophenoxy)diphenylsulfones\textsuperscript{10} and respectively of various aromatic dichlorides containing ether ketone units.\textsuperscript{11}

Both 1-methoxynaphthalene and 1-ethoxynaphthalene dimerize in the presence of an oxidizing Lewis acid in nitrobenzene, to yield the corresponding 4,4'-dialkoxy-1,1'-binaphthyl.\textsuperscript{9,12} However, the corresponding alkoxy derivatives of benzene such as anisole were reported to produce only very low yields of 4,4'-dialkoxybiphenyl.\textsuperscript{13} So far, Scholl reaction has been successfully applied to the polymerization of α,ω-bis(1-naphthoxy)alkanes,\textsuperscript{13,14} 4,4'-bis(1-naphthoxy)diphenyl sulfone,\textsuperscript{9} and 4,4'-bis(1-naphthoxy)benzophenone.\textsuperscript{9}
However, there are no reported studies on the polymerization of difunctional phenoxy or phenylthio derivatives of diphenyl sulfone.

The first goal of this chapter is to describe the results on the Scholl polymerization of 4,4'-bis(phenoxy)diphenyl sulfone (1), of 1 substituted with various electron-donating groups, and of 4,4'-bis(phenylthio)diphenyl sulfone (2). The second goal is to discuss the structure-polymerizability relationship of the monomers based on the cation-radical reaction mechanism.

6.2. EXPERIMENTAL

6.2.1. Materials

Phenol (99+%), 2,3-dimethylphenol (97%), 3,5-dimethylphenol (99+%), 2,6-dimethylphenol (99.8+%), 3-tert-butylphenol (99%), 3,5-di-tert-butylphenol (99%), 2,3-dimethoxyphenol (98%), 2,6-dimethoxyphenol (99%), 2,6-diphenylphenol (97%), 5,6,7,8-tetrahydro-1-naphthol (99%) (all from Aldrich), thiophenol (97%) and 2,3,5-trimethylphenol (98%) (both from Lancaster Synthesis), 2-tert-butylphenol (>97%) and 3-methoxyphenol (97%) (both from Fluka) were used as received. 4,4'-Dichlorodiphenyl sulfone (98%, from Aldrich) was recrystallized twice from toluene. K$_2$CO$_3$ (Fisher) and anhydrous FeCl$_3$ (Aldrich) were used as received. Dimethyl sulfoxide (DMSO) (Fisher) was distilled from CaO. Nitrobenzene was distilled from CaH$_2$ under nitrogen. All other solvents were used as received.

6.2.2. Monomer Synthesis

The synthesis of the monomers is outlined in Scheme 6.1. All the monomers (1-14 in Table 6.1) were synthesized by the aromatic nucleophilic
displacement reaction of 4,4'-dichlorodiphenyl sulfone with the corresponding phenol or phenol derivative and thiophenol respectively. Reactions were performed in DMSO at 155°C, using K₂CO₃ as base. The resulting monomers were purified by either column chromatography or by recrystallization until their purity was greater than 99%. An example for the synthesis of 4,4'-bis(2,3-dimethoxyphenoxy)diphenyl sulfone is given as follows.

2,3-Dimethoxyphenol (9.500 g, 61.6 mmol) was dissolved in a mixture containing 85 mL DMSO and 28.3 mL toluene, and K₂CO₃ (10.220 g, 74 mmol) was added. The reaction flask was equipped with a nitrogen inlet, a thermometer, and a Dean Stark trap equipped with a condenser. The reaction mixture was heated at 155°C until the theoretical amount of water was collected. Then the mixture was allowed to cool to 70°C, and a solution of 4,4'-dichlorodiphenyl sulfone (8.142 g, 28.4 mmol) in 14.2 mL toluene was added. The reaction was heated up again to 155°C until all the toluene was collected in the Dean Stark trap. Afterwards, the reaction mixture was stirred at 155°C for 6 h. The cooled reaction mixture was poured into 2 L cold water, and neutralized with dilute HCl. The resulting precipitate was filtered and dissolved in 100 mL toluene, washed three times with 2 N aqueous NaOH solution, and then with water until neutral. The toluene layer was dried over anhydrous MgSO₄, and the toluene was removed on a rotovapor. The residue was purified twice by column chromatography (basic alumina, dichloromethane as eluent) to yield 6.500 g (44%) of a white solid, purity (HPLC): 99.2%. mp 108-110°C, 1H-NMR: 3.75 (s, Ar-OCH₃, 6H), 3.90(s, Ar-OCH₃', 6H), 6.67 (d, Ar-H, 2H), 6.83 (d, Ar-H, 2H), 6.98 (d, Ar-H, 4H), 7.07 (d, Ar-H, 2H) and 7.83 (d, Ar-H).
Scheme 6.1. Synthesis of 4,4'-bis(phenoxyl)diphenyl sulfone, its substituted derivatives, and 4,4'-bis(phenylthio)diphenyl sulfone monomers.
Table 6.1. Synthesis of 4,4'-Bis(Phenoxy)Diphenyl Sulfone, Its Derivatives, and 4,4'-Bis(Phenylthio)Diphenyl Sulfone.

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<tr>
<th>Monomer Notation</th>
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<th>Recrystallization Solvent</th>
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<th>R₂</th>
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<td>150-151</td>
<td>O</td>
<td>H</td>
<td>CH₂CH₂-</td>
<td>CH₂CH₂-</td>
<td>H</td>
</tr>
</tbody>
</table>

a) monomer was purified by column chromatography using silica gel column, chloroform as eluent.
b) monomer was purified twice by column chromatography using basic alumina column, dichloromethane as eluent.
Table 6.2. $^1$H-NMR (CDCl$_3$, $\delta$, ppm) Chemical Shifts of Diphenyl Sulfone Monomers.

<table>
<thead>
<tr>
<th>Monomer Notation</th>
<th>$\delta$, ppm</th>
</tr>
</thead>
<tbody>
<tr>
<td>1 A(Ar-H, 7.01, d, 4H), B(Ar-H, 7.04, d, 4H), C(Ar-H, 7.21, t, 2H), D(Ar-H, 7.40, t, 4H), E(Ar-H, 7.92, d, 4H)</td>
<td></td>
</tr>
<tr>
<td>2 A(Ar-H, 7.18, d, 4H), B+D(Ar-H, 7.34-7.61, m, 10H), E(Ar-H, 7.72, d, 4H)</td>
<td></td>
</tr>
<tr>
<td>3 A(Ar-H, 6.84, d, 4H), B(Ar-CH$_3$, 2.08, s, 12H), C(D(Ar-H, 7.11, s, 6H), E(Ar-H, 7.83, d, 4H)</td>
<td></td>
</tr>
<tr>
<td>4 A(Ar-H, 7.00, d, 4H), B(Ar-H, 6.66, s, 4H), C(Ar-H, 6.86, s, 2H), D(Ar-CH$_3$, 2.29, s, 12H), E(Ar-H, 7.86, d, 4H)</td>
<td></td>
</tr>
<tr>
<td>5 A(Ar-H, 6.89, d, 4H), B(Ar-H, 6.60, d, 2H), B'(Ar-CH$_3$, 2.06, s, 6H), C(Ar-H, 7.05, d, 2H), D(Ar-CH$_3$, 2.32, s, 6H), D'(Ar-CH$_3$, 2.26, s, 6H), E(Ar-H, 7.82, d, 4H)</td>
<td></td>
</tr>
<tr>
<td>6 A(Ar-H, 6.90, d, 4H), B(Ar-H, 6.63, s, 2H), B'(Ar-CH$_3$, 2.01, s, 6H), C(Ar-H, 6.89, s, 2H), D(Ar-CH$_3$, 2.27, s, 6H), D'(Ar-CH$_3$, 2.26, s, 6H), E(Ar-H, 7.83, d, 4H)</td>
<td></td>
</tr>
<tr>
<td>7 A(Ar-H, 7.03, d, 4H), B(Ar-H, 6.84, m, 2H), B'(Ar-C(CH$_3$)$_2$, s, 136, 18H), C(Ar-H, 7.13, m, 2H), D(Ar-H, 7.44, m, 2H), D'(Ar-H, 7.18, m, 2H), E(Ar-H, 7.89, d, 4H)</td>
<td></td>
</tr>
<tr>
<td>8 A(Ar-H, 7.01, d, 4H), B(Ar-H, 6.84, d, 2H), B'(Ar-H, 7.09, s, 2H), C(Ar-H, 7.27, d, 2H), D(Ar-H, 7.35, m, 2H), D'(Ar-C(CH$_3$)$_3$, s, 1.28, 18H), E(Ar-H, 7.87, d, 4H)</td>
<td></td>
</tr>
<tr>
<td>9 A(Ar-H, 7.00, d, 4H), B(Ar-H, 6.89, d, 4H), C(Ar-H, 7.28, t, 2H), D(Ar-C(CH$_3$)$_3$, 1.28, 18H), E(Ar-H, 7.87, d, 4H)</td>
<td></td>
</tr>
<tr>
<td>10 A(Ar-H, 7.03, d, 4H), B+D(Ar-H, 6.60-6.79, m, 6H), D(Ar-H, 7.27, m, 2H), D'(Ar-OCH$_3$, 3.79, s, 6H), E(Ar-H, 7.87, d, 4H)</td>
<td></td>
</tr>
<tr>
<td>11 A(Ar-H, 6.65, d, 4H), B(Ar-OCH$_3$, 3.77, s, 12H), C(Ar-H, 7.19, t, 2H), D(Ar-H, 6.91, d, 4H), E(Ar-H, 7.80, d, 4H)</td>
<td></td>
</tr>
<tr>
<td>12 A(Ar-H, 6.98, d, 4H), B(Ar-H, 6.83, d, 2H), B'(Ar-OCH$_3$, 3.75, s, 6H), C(Ar-H, 6.67, d, 2H), D(Ar-H, 7.07, d, 2H), D'(Ar-OCH$_3$, 3.90, s, 6H), E(Ar-H, 7.83, d, 4H)</td>
<td></td>
</tr>
<tr>
<td>13 A(Ar-H, 6.52, d, 4H), B+D(Ar-H, 7.29-7.53, m, 20H), C+D+E(Ar-H, 7.08-7.23, m, 10H)</td>
<td></td>
</tr>
<tr>
<td>14 A(Ar-H, 6.92, d, 4H), B(Ar-H, 6.75, d, 2H), B'(ArCH$_2$CH$_2$, 2.53, t, 4H), C(Ar-H, 6.98, d, 2H), D(Ar-H, 7.12, t, 2H), D'(ArCH$_2$CH$_2$, 2.80, t, 4H), E(Ar-H, 7.83, d, 4H), (Ar-CH$_2$CH$_2$CH$_2$Ar, 1.74, m, 8H)</td>
<td></td>
</tr>
</tbody>
</table>
6.2.3. Polymerization Reactions

The polymerization reaction is presented in Scheme 6.2. The results of the polymerizations are presented in Tables 6.3 - 6.7. All polymerizations were performed in dry nitrobenzene under a stream of nitrogen, by using anhydrous FeCl₃ as oxidant. The molar ratio of FeCl₃/monomer was maintained 4/1 in all experiments. An example is given as follows.

4,4'-Bis(2,3-dimethoxyphenoxy)diphenyl sulphone (0.523 g, 1 mmol) was dissolved in 2 mL dry nitrobenzene, to which a solution of anhydrous FeCl₃ (0.650, 4 mmol) in 1.5 mL dry nitrobenzene was added dropwise. The reaction mixture was stirred at room temperature for 17 h. The content was precipitated into 200 mL methanol acidified with 2% HCl. The precipitate was filtered, washed with boiling methanol and dried in vacuo to yield 0.195 g (37%) of polymer. $\overline{M}_n$ (GPC): 1600 g/mol, $\overline{M}_w/\overline{M}_n$=1.05.

6.3. RESULTS AND DISCUSSION

The diphenyl sulphone monomers were synthesized as shown in Scheme 6.1. Their synthesis consists of an aromatic nucleophilic displacement reaction of 4,4'-dichlorodiphenyl sulphone with phenol, thiophenol, and substituted phenol respectively. The reactions were performed in DMSO under N₂ atmosphere using K₂CO₃ as base. The structure of the monomers 1-14, their yields, purification methods, as well as their melting points are listed in Table 6.1.

200 MHz $^1$H-NMR spectroscopy was used to determine the structure of the monomers. The chemical shifts of their $^1$H-NMR spectra are listed in Table 6.2. They all agree with the expected structure.
Scheme 6.2 illustrates the polymerization reaction. The oxidative dehydrogenative polymerization of 4,4'-bis(phenoxy)diphenyl sulfone and 4,4'-bis(phenylthio)diphenyl sulfone are summarized in Table 6.3. All polymerizations were performed in dry nitrobenzene under nitrogen atmosphere. In order to achieve high molecular weight polymers the molar ratio of FeCl₃ to monomer was 4/1 in all polymerizations. No methanol insoluble polymer was obtained from the polymerization of 4,4'-bis(phenoxy)diphenyl sulfone (1), when the reaction was performed at room temperature (experiment 1, Table 6.3). However, when the reaction was conducted at 40°C, a 2% yield of methanol insoluble polymer fraction was obtained. The highest polymer yield (13%) was achieved in experiment 7 (Table 6.3) when the polymerization was performed at 100°C. When the polymerization reaction was performed in the presence of 0.032 mL of 1,4-dioxane (experiment 5, Table 6.3), the polymer yield decreased from 13% (experiment 6, Table 6.3) to 2%. Both the experiments 5 and 6 were performed at the same temperature and with the same concentrations of monomers and oxidant. As indicated in Table 6.3, all the poly(ether sulfone)s derived from 4,4'-bis(phenylthio)diphenyl sulfone are insoluble in CHCl₃ and tetrahydrofuran (THF). The polymers are however soluble in N,N-dimethylformamide (DMF) and N-methyl-2-pyrrolidinone (NMP). This solubility behavior is identical to that of the corresponding polymer synthesized by aromatic nucleophilic substitution of 4,4'-dichlorodiphenyl sulfone with 4,4'-biphenol.¹⁵,¹⁶

The polymerizations of 4,4'-bis(phenylthio)diphenyl sulfone are summarized as experiments 8-15 in Table 6.3. The polymerization at 25°C (experiment 9, Table 6.3) resulted in a polymer yield of 45%, with inherent viscosity of 0.10 dL/g. By increasing the reaction temperature to 75°C, the inherent
Scheme 6.2. Synthesis of polyether sulfones by the polymerization of 4,4'-bis(phenoxyl)diphenyl sulfone, its substituted derivatives, and 4,4'-bis(phenylthio)diphenyl sulfone monomers.
Table 6.3. Synthesis of Poly(Ether Sulfone)s from 4,4'-Bis(Phenoxy)Diphenyl Sulfone (1) and 4,4'-Bis(Phenylthio)-Diphenyl Sulfone (2).

<table>
<thead>
<tr>
<th>Exp. No.</th>
<th>Monomer/monol</th>
<th>PhNO₂ (mL)</th>
<th>FeCl₃ (mmol)</th>
<th>PhNO₂ (mL)</th>
<th>Reaction Temperature (°C)</th>
<th>Reaction Time (h)</th>
<th>Polymer Yield (%)</th>
<th>η_{inh}ᵃ (dL/g)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
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<tr>
<td>2</td>
<td>1/2.0</td>
<td>2.0</td>
<td>8.0</td>
<td>5.0</td>
<td>40</td>
<td>24</td>
<td>2ᵇ</td>
<td>-</td>
</tr>
<tr>
<td>3</td>
<td>1/2.5</td>
<td>2.0</td>
<td>10.0</td>
<td>5.5</td>
<td>60</td>
<td>24</td>
<td>3ᵇ</td>
<td>-</td>
</tr>
<tr>
<td>4</td>
<td>1/2.0</td>
<td>1.5</td>
<td>8.0</td>
<td>5.0</td>
<td>70</td>
<td>24</td>
<td>12ᵇ</td>
<td>-</td>
</tr>
<tr>
<td>5</td>
<td>1/4.0</td>
<td>3.0</td>
<td>16.0</td>
<td>7.0ᶜ</td>
<td>90</td>
<td>24</td>
<td>2ᵇ</td>
<td>-</td>
</tr>
<tr>
<td>6</td>
<td>1/2.0</td>
<td>1.5</td>
<td>8.0</td>
<td>3.5</td>
<td>90</td>
<td>24</td>
<td>13ᵇ</td>
<td>-</td>
</tr>
<tr>
<td>7</td>
<td>1/2.5</td>
<td>2.0</td>
<td>10.0</td>
<td>5.5</td>
<td>100</td>
<td>24</td>
<td>13ᵇ</td>
<td>-</td>
</tr>
<tr>
<td>8</td>
<td>2/1.0</td>
<td>2.0</td>
<td>4.0</td>
<td>0</td>
<td>25</td>
<td>10</td>
<td>35</td>
<td>0.11</td>
</tr>
<tr>
<td>9</td>
<td>2/1.0</td>
<td>2.0</td>
<td>4.0</td>
<td>2.5</td>
<td>25</td>
<td>22</td>
<td>45</td>
<td>0.10</td>
</tr>
<tr>
<td>10</td>
<td>2/1.0</td>
<td>1.0</td>
<td>4.0</td>
<td>2.5</td>
<td>40</td>
<td>3</td>
<td>44</td>
<td>0.12</td>
</tr>
<tr>
<td>11</td>
<td>2/1.0</td>
<td>1.0</td>
<td>4.0</td>
<td>1.5</td>
<td>40</td>
<td>3</td>
<td>48</td>
<td>0.12</td>
</tr>
<tr>
<td>12</td>
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<td>1.0</td>
<td>4.0</td>
<td>2.5ᵈ</td>
<td>40</td>
<td>14</td>
<td>34</td>
<td>0.01</td>
</tr>
<tr>
<td>13</td>
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<td>4.0</td>
<td>2.5</td>
<td>50</td>
<td>22</td>
<td>17</td>
<td>0.15</td>
</tr>
<tr>
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<td>2/1.0</td>
<td>1.5</td>
<td>4.0</td>
<td>1.8</td>
<td>50</td>
<td>22</td>
<td>18</td>
<td>0.17</td>
</tr>
<tr>
<td>15</td>
<td>2/1.0</td>
<td>2.0</td>
<td>4.0</td>
<td>1.5</td>
<td>75</td>
<td>24</td>
<td>24</td>
<td>0.23</td>
</tr>
</tbody>
</table>

ᵃ) measured at a concentration of 0.5 g/dL in DMSO at 25 °C.
b) insoluble in CHCl₃ and THF, but soluble in N,N-dimethylformamide (DMF) and 1-methyl-2-pyrrolidinone (NMP).
c) 0.032 mL 1,4-dioxane added.
d) half equivalent of FeCl₃ was replaced with BF₃OEt₂.
viscosity increases to 0.23 dL/g and the polymer yield decreases to 24%. The polymerization performed in the presence of a half equivalent of boron trifluoride etherate to FeCl₃, decreases both the polymer yield and the viscosity of the resulting polymer (experiment 12, Table 6.3).

In summary, all the polymers synthesized from 4,4'-bis(phenylthio)diphenyl sulfone (2) are soluble in DMSO. At the same reaction temperature and under similar experimental conditions (compare experiment 2 with 10-12, Table 6.3), the polymerization of 2 produced polymers of substantially higher yield than that of 4,4'-bis(phenoxo)diphenyl sulfone (1).

The most probable mechanism of polymerization has been considered to be a radical-cation mechanism. This mechanism was also suggested to be responsible for the dimerization of monosubstituted naphthalene derivatives. This polymerization mechanism is shown in Scheme 6.3. This mechanism can be used to understand the higher polymer yield obtained with the phenylthio derivative 2 than with the phenoxo derivative 1 of diphenyl sulfone. For monomers 1 and 2, \( R_1 = R_2 = R_3 = R_4 = H \).

The first step of the polymerization involves the oxidation of the respective monomers 15 by FeCl₃ to generate a cation-radical intermediate 16 (eq 3, Scheme 6.3). Since the sulfur atom in the diphenyl sulfide linkage in 2 (15, \( X = S \)) is more electron donating than the oxygen atom in 1 (15, \( X = O \)), monomer 2 has a lower oxidation potential than monomer 1. Therefore, monomer 2 has a higher rate constant in equation 3 from Scheme 6.3 than monomer 1 does.

The second step of this polymerization (eq 4, Scheme 6.3) represents the nucleophilic attack of monomer 15 on the electrophilic cation-radical intermediate 16. This reaction generates the 1,1'-dihydrobiphenyl intermediate 17 with the
Scheme 6.3. The cation-radical mechanism of polymerization of diphenyl sulfone derivatives.
radical and the cation delocalized in two separate phenyl rings. In equation 4, the monomer 2 (15, X = S) has a higher nucleophilicity than monomer 1 (15, X = O) due to the difference between the electron-donating capabilities of sulfur versus oxygen. This makes the rate constant of the nucleophilic attack by monomer 2 be higher than that of monomer 1 towards the cation-radical. However, the stronger electron-donating sulfur atom in the cation-radical 16 derived from 2 also stabilizes and therefore deactivates this radical-cation more than corresponding 16 containing oxygen (derived from monomer 1). This would decrease the reactivity of 16 (X = S) in the reaction from equation 4 by comparison with that of 16 with X = O. Experimental results have indicated that monomer 2 (15, X = S) has consistently produced polymers in higher yields than monomer 1 (15, X = O). This indicates that the difference between the nucleophilicities of the two monomers is larger than the difference between the reactivities of the two propagating species, therefore, the nucleophilicity of 15 is the dominating factor in determining the rate constant of eq 4. The reactions shown in equations 3 and 4 are the slowest steps in the overall polymerization reactions. It is therefore reasonable to conclude that the monomer with higher nucleophilicity will be more reactive as determined by the combined nucleophilicity effects on these reactions (equation 3 and 4, Scheme 6.3). Accordingly, monomer 2 (i.e. 15, X = S) exhibits a higher polymerizability than monomer 1 (i.e. 15, X = O).

Alternatively, the cation-radical 16 can act as a radical and dimerize to the dication 18 (eq 5, Scheme 6.3), which releases one proton in both equations 6 and 7 to form a neutral dimer molecule 20. However, since cation-radical 16 is generated in low concentrations due to the dropwise addition of the oxidant (FeCl₃), we believe that the dimerization outlined in eq 5 is a less important reaction than the
electrophilic attack shown in eq 4. The dimeric radical cation 17 releases one proton and gives a dimer radical 21 (eq 8, Scheme 6.3), which is subsequently oxidized to a dimer cation 19 (eq 9, Scheme 6.3). The release of a proton from 19 leads to a neutral dimer molecule 20 as shown in eq 7. The subsequent repetition of eqs 3, 4, 8, 9 and 7 on the dimer and higher homologues generates polymer molecules containing both diphenyl sulfone units and biphenyl units in the backbone.

Based on the discussion on the polymerization mechanism, it is expected that the low yields obtained in the polymerization of 4,4'-bis(phenoxy)diphenyl sulfone can be increased by introducing electron-donating groups on the phenoxy ring. On the other hand, the introduction of substituents can also increase the solubility of the resulting polymer in common organic solvents. Therefore, a systematic approach has been taken to polymerize the monomers 3-14 which have various substituents in the phenoxy group.

The first group of monomers is based on methyl substituted 4,4'-bis(phenoxy)diphenyl sulfone. The results of polymerization and of polymer characterization are summarized in Table 6.4. All the polymers are soluble in common organic solvents such as CHCl₃ and THF. The polymerization of 4,4'-bis(2,6-dimethylphenoxy)diphenyl sulfone (3) leads to up to 74% polymer yield. However, all polymers resulted from 3 have low molecular weights (1300-2200 g/mol). A representative 200 MHz ¹H-NMR spectrum of poly(3) is shown in Figure 6.1 along with the assignment of its protonic resonances. Besides all the expected resonances, a proton resonance at 7.17 ppm was observed. This was assigned to the chloride anion terminated chain end. Based on the molecular weight determined by GPC (Mₙ = 2200, experiment 2 in Table 6.4), the calculated chlorine
Table 6.4. Synthesis of Poly(Ether Sulfone)s from 4,4'-Bis(2,6-Dimethylphenoxy)Diphenyl Sulfone (3), 4,4'-Bis(3,5-Dimethylphenoxy)Diphenyl Sulfone (4), 4,4'-Bis(2,3-Dimethylphenoxy)Diphenyl Sulfone (5), and 4,4'-Bis(2,3,5-Trimethylphenoxy)Diphenyl Sulfone (6).

<table>
<thead>
<tr>
<th>Exp. No.</th>
<th>Monomer Solution</th>
<th>FeCl₃ Solution</th>
<th>Reaction Temperature (°C)</th>
<th>Reaction Time (h)</th>
<th>Polymer Yield (%)</th>
<th>( \overline{M}_n ) (g/mol)</th>
<th>( \overline{M}_\text{w}/\overline{M}_n )</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>3/2.2 2.0</td>
<td>8.8 9.0</td>
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<td>-</td>
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<td>1/12</td>
<td>60</td>
<td>2200</td>
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</tr>
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<td>4.0 2.5</td>
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<td>22</td>
<td>1</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
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<td>4.0 2.5</td>
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<td>281.93^c</td>
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<td>35</td>
<td>800</td>
<td>1.38</td>
</tr>
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<td>25</td>
<td>7</td>
<td>9</td>
<td>1700</td>
<td>1.39</td>
</tr>
</tbody>
</table>

a) 1/2 equivalent FeCl₃ was replaced with BF₃OEt₂.
b) multi-modal molecular weight distribution over a broad molecular weight range was observed on GPC chromatogram.
c) multi-modal molecular weight distribution over a broad molecular weight range was observed on GPC chromatogram.

The GPC trace of this polymer is shown in Figure 6.3.
Figure 6.1. 200 MHz $^1$H-NMR spectrum (CDCl$_3$) of poly[4,4'-bis(2,6-dimethylphenoxy)diphenyl sulfone] (Sample No. 2, Table 6.4).
content is 3.2%. Elemental analysis performed on the same sample gives a chlorine content of 2.6%. Therefore, this polymer contains chlorine chain ends as a result of the termination reaction represented in Scheme 6.4. This termination reaction results from the attack of the chloride part of the counter anion (presumably FeCl$_4^-$) as a nucleophile on the cation-radical 22 to generate the 4-chlorophenyl radical intermediate 23 (eq 11, Scheme 6.4). The subsequent oxidation of 23 (eq 12) followed by the release of a proton leads to the formation of a 4-chlorophenoxy terminated chain end 25 (eq 13). Due to the electron-withdrawing character of the 4-chloro substituent, this chain end is oxidized only with difficulty and therefore, it represents an unreactive, dead chain end. This process limits the molecular weight of the resulting polymer.

The polymerization of 4,4'-bis(3,5-dimethylphenoxy)diphenyl sulfone (4) results only in very low polymer yields. The $^1$H-NMR spectrum of poly(4) is shown in Figure 6.2. No chlorine-substituted chain end can be observed. However, the 3,5-dimethylphenoxy chain ends were suggested by the resonances present at 6.66 and 6.89 ppm. The absence of chloride termination may be due to the steric hindrance of the 4-position in the phenoxy group of monomer 4 by the two methyl groups from its 3,5-positions.

The polymerization of 4,4'-bis(2,3-dimethylphenoxy)diphenyl sulfone (5) produced only polymers with a multi-modal molecular weight distribution. A typical GPC chromatogram of these polymers is shown in Figure 6.3. About 26% of the poly(5) has $\bar{M}_n > 250,000$ g/mol with peak molecular weight of 900,000 g/mol. The fraction of $\bar{M}_n$ between 20,000 and 250,000 represents 21% of the total polymer. However, the polymer is very soluble in chloroform. The $^1$H-NMR spectrum of the same poly(5) sample is shown in Figure 6.4. This polymer
Scheme 6.4. The mechanism of termination reaction occurring during the polymerization of 4,4'-bis(2,6-dimethylphenoxy)diphenyl sulfone.
Figure 6.2. 200 MHz $^1$H-NMR spectrum (CDCl$_3$) of poly[4,4'-bis(3,5-dimethylphenoxy)diphenyl sulfone] (Sample No. 8, Table 6.4).
Figure 6.3. A typical GPC chromatogram of poly[4,4'-bis(2,3-dimethylphenoxy)diphenyl sulfone (Sample No. 10, Table 6.4).
Figure 6.4. 200 MHz $^1$H-NMR spectrum (CDCl$_3$) of poly[4,4-bis(2,3-dimethylphenoxy)diphenyl sulfone] (Sample No. 10, Table 6.4).
displays a resonance at 3.97 ppm. The addition of D$_2$O to the NMR sample tube does not shift this resonance. The resonance at 3.97 ppm is absent in all polymers derived from 3 and 4, therefore it was assigned to the diphenylmethane group which results from the side reactions of the methyl groups of 5.

A possible mechanism for this side reaction is shown in Scheme 6.5. It involves the formation of a benzyl radical 27 by releasing one of the benzylic protons from the radical-cation 26 (eq 15, Scheme 6.5). The subsequent oxidation of 27 leads to the benzyl cation 28 (eq 16). The benzyl cation 28 acts as an electrophile and reacts with the monomer 6 to form a diphenylmethane structure 29 (eq 17). Structure 28 can also attack a polymer backbone to generate a branched polymer. Intermediate 29 releases one proton and forms a neutral diphenylmethane structure 30 (eq 18). The alternative pathway for the generation of diphenylmethane structure 30 is shown in eq 19 from Scheme 6.5. In this reaction, a radical-radical coupling takes place between the benzyl radical 27 (generated in eq 15) and the radical of the radical-cation 26. The other possible reaction is shown in eq 20. The benzyl cation 28 combines with the chloride anion part of the counter anion (presumably FeCl$_4^-$) leading to a benzyl chloride 31. The $^1$H-NMR spectrum of poly(5) (Figure 6.4) does not show resonances corresponding to benzyl chloride units. Therefore if benzyl chloride groups are generated through eq 20, in the presence of FeCl$_3$ they react with various nucleophilic moieties leading to structures of type 29 obtained through eq 17. The other possible reaction is shown in eq 21 from Scheme 6.5, i.e. the radical-radical coupling between two benzyl radicals 27, which leads to 1,2-diphenylethane structure 32. However, the $^1$H-NMR spectrum of poly(5) does not show any resonance corresponding to structure 32. This is due to the low concentration of the benzyl radical 27, which is a very reactive
Scheme 6.5. A proposed mechanism for the side reaction involving benzyl cation/benzyl radical during the polymerization of 4,4'-bis(2,3-dimethylphenoxy)diphenyl sulfone.
intermediate and is consumed by other reactions as shown in eq 16 and 19 from Scheme 6.5. Therefore, during this polymerization process eq 21 is probably a less likely side reaction.

The benzyl radical/benzyl cation side reactions do not occur in the case of 4,4'-bis(2,6-dimethylphenoxy)diphenyl sulfone (3). This is due to the fact that the 2,6-dimethyl groups are located ortho to the phenoxy group. This increases the electron density at these 2,6-positions. The enhanced electron density on the 2,6-positions makes the C-H bond in the methyl groups stronger, and therefore the release of a proton to generate the benzyl radical is more difficult.

The benzyl cation has been repeatedly proposed as an intermediate in the anodic oxidation of toluene,17 p-xylene,18 mesitylene,18 1,2,4-trimethylbenzene,19 durene,18 1,2,3,5-tetramethylbenzene,19 and pentamethylbenzene.19 The benzyl cation intermediate generates diphenylmethane,17-21 or reacts with water to form benzyl alcohol.22 A similar intermediate was also proposed to occur during the oxidative reactions of methylnaphthalene.23

The polymerization of 4,4'-bis(2,3,5-trimethylphenoxy)diphenyl sulfone (6) produces polymers with $M_n$ up to 1900 g/mol. The $^1$H-NMR spectrum of the poly(6) does not show 4-chloro-2,3,5-trimethylphenoxy chain ends. The only identified chain end is based on the 2,3,5-trimethylphenoxy group. The $^1$H-NMR spectrum of poly(6) indicates also that the propagation reaction proceeds through the 4-position of the 2,3,5-trimethylphenoxy group. It is apparent that the 4-position of 2,3,5-trimethylphenoxy group is sterically hindered and therefore, this monomer leads only to very low polymer conversions. At the same time the presence of three methyl groups in 4,4'-bis(2,3,5-trimethylphenoxy)diphenyl
sulfone (6) enhances the overall electron density on the phenoxy ring and thus decreases the probability to form the benzyl radical by proton release.

In summary, the methyl substituted 4,4'-bis(phenoxy)diphenyl sulfone monomers (3-6) lead to higher polymer yields than the unsubstituted monomer 4,4'-bis(phenoxy)diphenyl sulfone (1). All polymers resulted from methyl substituted monomers are soluble in common organic solvents. However, the molecular weights of the polymers are low due to termination reaction with the chloride part of the counter anion as shown for the 2,6-dimethylphenoxy substituted monomer 3. Side reactions which lead to propagation through the benzyl cation/benzyl radical are observed for monomer 5.

In order to avoid the side reaction of the benzyl cation/benzyl radical, the tert-butyl substituted monomers 7 to 9 were investigated since the benzyl radical and the subsequent benzyl cation can not be generated from the tert-butyl substituent. These polymerization experiments are summarized in Table 6.5. Only 4,4'-bis(2-tert-butylphenoxy)diphenyl sulfone (7) produces polymers with $\bar{M}_n$ up to 1900 g/mol. The 200 MHz $^1$H-NMR spectrum of a typical poly(7) is shown in Figure 6.5. As expected, the polymerization of 7 does not lead to the reaction which occurs in the case of methyl-substituted monomer 5. No polymers could be obtained under a variety of experimental conditions from the corresponding 3-tert-butylphenoxy derivatives 8 and 3,5-di-tert-butylphenoxy derivative 9. These results are presumably due to the steric hindrance at the 4-position of the phenoxy group of the monomer. This steric hindrance is caused by the presence of one (in monomer 8) and two (in monomer 9) tert-butyl groups.

The next electron-donating group which was attached to the phenoxy moiety of the monomer 1 is methoxy. Methoxy is more electron-donating than
Table 6.5. Synthesis of Poly(Ether Sulfones) from 4,4'-Bis(2-tert-Butylphenox)Diphenyl Sulfone (7), 4,4'-Bis(3-tert-Butylphenox)Diphenyl Sulfone (8), and 4,4'-Bis(3,5-Di-tert-Butylphenox)Diphenyl Sulfone (9).

<table>
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<tr>
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<th>FeCl₃ (mmol)</th>
<th>PhNO₂ (mL)</th>
<th>Reaction Temperature (°C)</th>
<th>Reaction Time (h)</th>
<th>Polymer Yield (%)</th>
<th>$M_n$ (g/mol)</th>
<th>$M_w$/$/M_n$</th>
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Figure 6.5. 200 MHz $^1$H-NMR spectrum (CDCl$_3$) of poly[4,4'-bis(2-tert-butylphenoxy)diphenyl sulfone] (Sample No. 1, Table 6.5).
methyl, yet has no labile hydrogens to cause the side reaction generated through the benzyl cation/benzyl radical. Methoxy also does not impart steric hindrance like the tert-butyl group. Three methoxy derivatives of 4,4'-bis(phenoxo)diphenyl sulfone (1) have been synthesized and polymerized. Their polymerization results are summarized in Table 6.6. The 4,4'-bis(3-methoxyphenoxo)diphenyl sulfone (10) leads to up to 44% polymer yield when the polymerization is carried out at room temperature. However, the resulting polymers are insoluble in chloroform and THF. They are soluble in N-methyl-2-pyrrolidinone (NMP) and N,N-dimethylformamide (DMF).

The polymerization of 2,6-dimethoxyphenoxo derivative 11 leads to polymer yields as high as 76%, and $M_n$ up to 2200 g/mol. The 2,3-dimethoxyphenoxo monomer 12 also produces polymer yields of up to 58%. A representative 200 MHz $^1$H-NMR spectrum of poly(12) is shown in Figure 6.6. However, the assignments made based on the chemical shift of monomer 12 (Table 6.2) indicate that the polymer is generated through crosscoupling at the 5,5'-positions rather than through normal 4,4'-linkage. This result is expected when the higher electron-donating power of methoxy groups is taken into consideration. The 4-position is close to the 3-methoxy group and therefore is subjected to some steric hindrance. The 5-position is in para position versus the 2-methoxy group. This is the position with the highest electron density and also free from steric hindrance. Therefore, the polymerization of 12 proceeds through coupling at the positions 5,5' of the phenoxo group.

4,4'-Bis(2,6-diphenylphenoxo)diphenyl sulfone (13) has also been polymerized. The polymerization results of 13 are listed in Table 6.7. This polymerization is relatively slow. After 36 h of polymerization at room temperature
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<th>Reaction Temperature (°C)</th>
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a) insoluble in CHC₃ and THF, but soluble in DMF and NMP.
Figure 6.6. 200 MHz $^1$H-NMR spectrum (CDCl$_3$) of poly[4,4'-bis(2,3-dimethoxyphenoxy)diphenyl sulfone] (Sample 9, Table 6.6).
Table 6.7. Synthesis of Poly(Ether Sulfones) from 4,4'-Bis(2,6-Diphenylphenoxy)Diphenyl Sulfone (13) and 4,4'-Bis(5,6,7,8-Tetrahydro-1-Naphthoxy)Diphenyl Sulfone (14).

<table>
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<tr>
<th>Exp. No.</th>
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<th>PhNO₂ (mL)</th>
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<th>PhNO₂ (mL)</th>
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<th>Reaction Time (h)</th>
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we obtained a polymer yield of 36%. Both the polymer yield and the polymer molecular weight increase as the polymerization temperature is raised from 25°C to 60°C. A representative 200 MHz $^1$H-NMR spectrum of poly(13) is shown in Figure 6.7. The chemical shifts of doublets A and B are shifted 0.4 ppm and 0.6 ppm upfield as compared to the corresponding chemical shifts in the monomer 3. Due to steric reasons the 2,6-diphenyl groups of 13 are not in the same plane with the central phenoxy ring. The tilt of the phenyl rings from the 2- and 6-positions in the radical-cation derived from 13 is shown in Figure 6.8. Consequently, the corresponding cation-radical intermediate (Figure 6.8) can not delocalize its charge over the two phenyl rings from the positions 2- and 5-. Therefore, these polymerizations (experiments 1-3, Table 6.7) failed to lead to polymers of high molecular weight.

The polymerization of 4,4'-bis(2,3-dimethylphenoxy)diphenyl sulfone (5) yields side reactions through the benzyl cation/radical. Consequently, we have synthesized the monomer 4,4'-bis(5,6,7,8-tetrahydro-1-naphthoxy)diphenyl sulfone (14), which resembles 5 in respect to its substitution position and nature of the dialkyl substituents. The polymerization results of 14 are summarized in Table 6.7. The polymerization of 14 leads to 38% polymer yield, with molecular weights in the range of 1500-1600 g/mol. A representative 200 MHz $^1$H-NMR spectrum of a typical poly(14) is shown in Figure 6.9. As expected, no diphenylmethane structure can be observed. Even though there are protons at the benzyl groups from the 5 and 8-positions, these positions are part of the 6-membered ring. If cyclic benzyl cations/benzyl radicals are generated, the subsequent reactions of these cyclic benzyl cations or benzyl radicals do not occur most probably due to steric reasons. Analysis of poly(14) by $^1$H-NMR spectroscopy did not show the presence of
Figure 6.7. 200 MHz $^1$H-NMR spectrum (CDCl$_3$) of poly[4,4'-bis(2,6-diphenylphenoxy)diphenyl sulfone (Sample 2, Table 6.7).
Figure 6.8. A schematic representation of the spatial conformation of the radicalcation derived from 4,4'-bis(2,6-diphenylphenoxy)diphenyl sulfone.
Figure 6.9. 200 MHz $^1$H-NMR spectrum (CDCl$_3$) of poly[4,4'-(5,6,7,8-tetrahydro-1-naphthoxy)]diphenyl sulfone (Sample No. 4, Table 6.7).
structural units derived from benzyl cation or benzyl radical side reactions. Therefore, the introduction of cyclic substituents on the phenoxy units can prevent the benzyl cation/benzyl radical side reactions.

The polymerization of 4,4'-bis(phenoxy)diphenyl sulfone substituted with methyl, tert-butyl, methoxy, and phenyl as electron-donating groups have increased the polymer yields and the solubility of the resulting polymers. However, with the exception of the monomer undergoing side reactions through the benzyl cation/benzyl radical intermediate, under present polymerization conditions, the other substituted phenoxy based monomers failed to produce polymers of high molecular weight.

Phenoxy and substituted phenoxy derivatives, which can not stabilize the radical-cation intermediate 15 through resonance lead to low molecular weight polymers. If the polymerization proceeds by the mechanism from eq 4 of Scheme 4.3, there are two reactions which are responsible for this. During all these experiments we maintained the same nucleophilicity for the counter-anion and change only the reactivity of the radical-cation and the nucleophilicity of the monomers. Therefore, the radical-cation reacts with either the monomer or with a fragment of the counter-anion (presumably Cl\textsuperscript{-}) or with both. Highly reactive radical-cation growing species are generated from non-nucleophilic monomers and therefore they react predominantly with the Cl\textsuperscript{-} fragment of the counter-anion. The polymerization of 4,4'-bis(1-naphthoxy)diphenyl sulfone monomer is capable of producing high yields of polymers with high molecular weight.\textsuperscript{9} Therefore, resonance stabilization represents an important parameter which should be considered in the selection of monomer structures for this type of radical-cation polymerization. Additional parameters which should be considered are the
oxidizing capability of the oxidant and the nucleophilicity of the counter-anion. These last two parameters are presently under investigation and will represent the subject of further publications.

6.4. CONCLUSIONS

4,4'-Bis(phenoxo)diphenyl sulfone (1), its derivatives with various electron-donating substituents (i.e. methyl, tert-butyl, methoxy, and phenyl), 4,4'-bis(phenylthio)diphenyl sulfone (2), and 4,4'-bis(5,6,7,8-tetrahydro-1-naphthoxy)diphenyl sulfone (14) have been polymerized under Scholl reaction conditions yielding polymers of relatively low molecular weight. 4,4'-Bis(phenylthio)diphenylsulfone (2) exhibits higher polymerizability than 4,4'-bis(phenoxo)diphenyl sulfone (1), due to the fact that 2 is more nucleophilic and therefore the monomer is more reactive while the growing species are less reactive.

Due to the termination of radical-cation intermediate with the Cl⁻ part of the counter anion (presumably FeCl₄⁻) poly[4,4'-bis(2,6-dimethylphenoxy)diphenyl sulfone]s can be synthesized only with low molecular weights. Poly[4,4'-bis(2,3-dimethylphenoxy)diphenyl sulfone]s have a high molecular weight fraction, which is generated by the side reactions involving benzyl cation/benzyl radical intermediates. Poly[4,4'-bis(2,3,5-trimethylphenoxy)diphenyl sulfone]s do not contain structural units derived from the Cl⁻ termination and the benzyl cation/benzyl radical side reactions. However, their molecular weights are very low presumably due to the steric hindrance at the 4-positions of the phenoxy ring.

4,4'-Bis(phenoxo)diphenyl sulfone monomer substituted by 2-tert-butyl group eliminates the side reaction involving benzyl cation/benzyl radical. However,
3-tert-butyl and 3,5-di-tert-butyl groups provide enough steric hindrance to prevent these two monomers from polymerization.

The monomers with 4,4'-bis(phen oxy)diphenyl sulfone substituted with a variety of methoxy groups on the phenyl ring increase the nucleophilicity of the monomers without introducing steric hindrance and subsequently lead to polymers free of structural units generated by the benzyl cation/benzyl radical side reactions.

Due to the tilt of the 2,6-diphenyl rings with respect to the phenoxy ring, 4,4'-bis(2,6-diphenylphenoxy)diphenyl sulfone does not provide enough resonance stabilization of its corresponding radical-cation and therefore, leads only to polymers of low molecular weights. 4,4'-Bis(5,6,7,8-tetrahydro-1-naphthoxy)diphenyl sulfone eliminates the benzyl cation/benzyl radical side reactions which occur in the polymerization of a similarly substituted 4,4'-bis(2,3-dimethylphenoxy)diphenyl sulfone monomer.

REFERENCES


CHAPTER 7

ON THE POLYMERIZABILITY OF 1,5-BIS(PHENOXY)PENTANES AND 1,5-BIS(PHENYLTHIO)PENTANE

7.1. INTRODUCTION

The homocoupling of bisaryloxy derivatives by Scholl reaction\textsuperscript{1,2} and of dihaloarylates by Ni\textsuperscript{9} catalyzed reactions\textsuperscript{3,4} represent novel approaches to the synthesis of various functional aromatic polyethers such as poly(ether sulfone)s\textsuperscript{1,2,3} and poly(ether ether ketone)s.\textsuperscript{1,4} The polymerization by the Scholl reaction led to the synthesis of high molecular weight polymers from either 4,4'-bis(1-naphthoxy)diphenyl sulfone,\textsuperscript{1} 4,4'-bis(1-naphthoxy)benzophenone,\textsuperscript{1} or α,ω-bis(1-naphthoxy)alkanes.\textsuperscript{5} However, the polymerization of 4,4'-bis(phenoxy)diphenyl sulfone, 4,4'-bis(phenoxy)diphenyl sulfone substituted with various electron-donating groups, and 4,4'-bis(phenylthio)diphenyl sulfone produced only polymers of low molecular weights.\textsuperscript{2} The low polymerizability of bis(phenoxy) and bis(phenylthio) monomers was considered to be caused by the low oxidizability of the phenoxy and phenylthio groups as compared with those of the naphthoxy polymerizable groups from the bis(1-naphthoxy) monomers.\textsuperscript{1,5}

In order to understand the polymerizability of the monomers in the cation-radical polymerization by Scholl reaction, 1,5-bis(phenoxy)pentane, 1,5-bis(phenoxy)pentane substituted with various electron-donating groups, and 1,5-bis(phenylthio)pentane were synthesized and polymerized under the oxidative reaction conditions. This chapter presents the results of these polymerizations and
discusses the cation-radical reactions of these monomers. The reactivity of these monomers will be compared with that of their aromatic counterparts which were discussed in Chapter 6.

7.2. EXPERIMENTAL

7.2.1. Materials

Phenol (99+%), 2,3-dimethylphenol (97%), 3,5-dimethylphenol (99+%), 2,6-dimethylphenol (99.8+%), 3-terr-butylphenol (99%), 3,5-di-terr-butylphenol (99%), 2,6-dimethoxyphenol (99%), 1,5-dibromopentane (97%) (all from Aldrich), thiophenol (97%) and 2,3,5-trimethylphenol (98%) (both from Lancaster Synthesis), 2-terr-butylphenol (>97%) and 3-methoxyphenol (97%) (both from Fluka) were used as received. KOH (Fisher) and anhydrous FeCl₃ (Aldrich) were used as received. Dimethyl sulfoxide (DMSO) (Fisher) was distilled from CaO. Nitrobenzene was distilled from CaH₂ under nitrogen. All other solvents were used as received.

7.2.2. Synthesis of Monomers

The synthesis of monomers 1-11 is outlined in Scheme 7.1. It consists of the nucleophilic substitution of 1,5-dibromopentane with the corresponding phenol, phenol derivative, or thiophenol respectively. All reactions were performed in dimethyl sulfoxide (DMSO) at 80°C, using KOH as base. The resulting monomers were purified by either vacuum distillation or recrystallization from acetone-methanol. An example for the synthesis of 1,5-bis(3-methoxyphenyl)pentane is provided as follows.
Scheme 7.1. Synthesis of 1,5-bis(phenoxyc)pentane (1), its substituted derivatives (3-11), and 1,5-bis(phenylthio)pentane (2) monomers.
3-Methoxyphenol (19.9 g, 0.16 mol) was dissolved in 60 mL DMSO, and an aqueous KOH solution (10.6 g, 0.19 mol KOH in 10 mL water) was subsequently added. The reaction mixture was heated to 45°C after which a solution of 1,5-dibromopentane (18.4 g, 0.08 mol) in 25 mL DMSO was added. The reaction was continued at 80°C for 6 h. The reaction mixture was cooled to room temperature and poured into 1 L of water. The resulting mixture was extracted 3 times with CHCl₃. The evaporation of chloroform layer yielded a residue which was recrystallized from acetone-methanol to yield 16.5 g (65%) of needle-like crystals. Purity (HPLC): >99.9%. M.p.: 41-42°C. ¹H-NMR (CDCl₃, δ, ppm): 1.71 (m, 2H, CH₂), 1.91(m, 4H, CH₂), 3.79 (m, 6H, Ar-OCH₃), 3.98 (t, 4H, -OCH₂), 6.48 (m, 6H, 2-, 4-, and 6-H of the phenoxyl unit), 7.18 (t, 2H, 5-H of the phenoxyl unit).

7.2.3. Polymerizations

All polymerization experiments were performed in dry nitrobenzene under nitrogen, by using anhydrous FeCl₃ as oxidant. An example is given as follows.

1,5-Bis(3,5-dimethylphenoxy)pentane (0.312 g, 1mmol) was dissolved in 1 mL dry nitrobenzene, to which a solution of anhydrous FeCl₃ (0.490 g, 3 mmol) in 2.0 mL dry nitrobenzene was added dropwise. The reaction mixture was stirred vigorously at room temperature for 20 h. The content was precipitated into 200 mL methanol acidified with 2% of concentrated aqueous hydrochloric acid. The precipitate was filtered, washed with boiling methanol and dried under vacuum to yield 0.040 g (13%) of polymer. Mn (GPC) = 5000 g/mol, Mw/Mn = 10.2.
Table 7.1. Synthesis of 1,5-Bis(Phenoxy)Pentane, Its Derivatives, and 1,5-Bis(Phenylthiol)Pentane.

![Chemical Structure](image)

<table>
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<th>Monomer Notation</th>
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<th>bp/Pressure °C/Torr</th>
<th>mp °C</th>
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<th>R₁</th>
<th>R₂</th>
<th>R₃</th>
<th>R₄</th>
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<td>OCH₃</td>
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<td>OCH₃</td>
<td>OCH₃</td>
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Table 7.2. $^1$H-NMR (CDCl$_3$, $\delta$, ppm) Chemical Shifts of 1,5-Bis-substituted Pentane Derivatives.

<table>
<thead>
<tr>
<th>Monomer Notations</th>
<th>$\delta$, ppm</th>
</tr>
</thead>
<tbody>
<tr>
<td>I</td>
<td>A(CH$_3_1$, 1.66, m, 2H), B(CH$_2$, 1.86, m, 4H), C(OCH$_2$, 3.99, t, 4H), D+F(Ar-H, 6.91-6.98, m, 6H), E(Ar-CH$_2$, 7.28, t, 4H)</td>
</tr>
<tr>
<td>2</td>
<td>A+B(CH$_3$, 1.57, m, 6H), C(SCH$_2$, 2.84, t, 4H), D+E+F(Ar-H, 7.11-7.30, m, 10H)</td>
</tr>
<tr>
<td>3</td>
<td>A+B(CH$_2$, 1.66-2.09, m, 6H), C(OCH$_2$, 3.80, t, 4H), D(Ar-CH$_3$, 2.29, s, 12H), E(Ar-H, 6.92, t, 2H), F(Ar-H, 7.02, d, 4H)</td>
</tr>
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<td>4</td>
<td>A(CH$_2$, 1.52, m, 2H), B(CH$_2$, 1.92, m, 4H), C(OCH$_2$, 3.95, m, 4H), D(Ar-H, 6.54, s, 4H), E(Ar-H, 6.59, s, 2H), F(Ar-CH$_3$, 2.29, s, 12H)</td>
</tr>
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</tr>
<tr>
<td>6</td>
<td>A(CH$_2$, 1.72, m, 2H), B(CH$_2$, 1.91, m, 4H), C(OCH$_2$, 3.96, t, 4H), D(Ar-H, 6.53, s, 2H), E(Ar-H, 6.61, s, 2H), F(Ar-CH$_3$, 2.28, s, 6H), F(Ar-CH$_3$, 2.23, s, 6H)</td>
</tr>
<tr>
<td>7</td>
<td>A(CH$_2$, 1.80, m, 2H), B(CH$_2$, 1.93, m, 4H), C(OCH$_2$, 4.03, t, 4H), D(Ar-H, 6.87, d, 2H), D'(Ar-C(CH$_3_3$, 1.40, s, 18H)</td>
</tr>
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<td>A(CH$_2$, 1.60, m, 2H), B(CH$_2$, 2.00, m, 4H), C(OCH$_2$, 3.99, t, 4H), D(Ar-H, 6.72, d, 2H), E(Ar-H, 6.98, d, 2H), F(Ar-H, 7.22, t, 2H), F'(Ar-C(CH$_3_3$, 1.34, s, 18H)</td>
</tr>
<tr>
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<td>A(CH$_2$, 1.63, m, 2H), B(CH$_2$, 1.71, m, 4H), C(OCH$_2$, 4.01, t, 4H), D(Ar-H, 6.77, s, 4H), E(Ar-H, 7.03, s, 2H), F(Ar-C(CH$_3_3$, 1.32, s, 36H)</td>
</tr>
<tr>
<td>10</td>
<td>A(CH$_2$, 1.71, m, 2H), B(CH$_2$, 1.91, m, 4H), C(OCH$_2$, 3.98, t, 4H), D+E+F(Ar-H, 6.48-6.53, m, 6H), F(Ar-H, 7.18, t, 2H), F(Ar-OCH$_3$, 3.79, m, 6H)</td>
</tr>
<tr>
<td>11</td>
<td>A(CH$_2$, 1.65, m, 2H), B(CH$_2$, 1.85, m, 4H), C(OCH$_2$, 4.00, t, 4H), D(Ar-OCH$_3$, 3.82, s, 12H), E(Ar-H, 6.97, t, 2H), F(Ar-H, 6.55, d, 12H)</td>
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7.3. RESULTS AND DISCUSSION

1,5-Bis(phenoxypentane, its substituted derivatives, and 1,5-bis(phenylthio)pentane monomers 1-11 were synthesized as presented in Scheme 7.1. The structure of monomers 1-11, their yields and melting points/boiling points are summarized in Table 7.1. The structure of the monomers is supported by their 200 MHz $^1$H-NMR spectra. The chemical shifts and the assignments of their $^1$H-NMR spectra are listed in Table 7.2. The $^1$H-NMR spectra of these monomers agree with the expected structures.

The cation-radical polymerization is shown in eq 2 from Scheme 7.2. All polymerization experiments were performed in dry nitrobenzene using FeCl$_3$ as the oxidant.

The polymerization results of 1,5-bis(phenoxypentane (1) and 1,5-bis(phenylthio)pentane (2) are summarized in Table 7.3. The polymerization of 1 at room temperature resulted in a 29% polymer yield (experiment 1, Table 7.3). Polymer yield increased to 36% by performing the polymerization at an elevated temperature, i.e. $60^\circ$C (experiment 2, Table 7.3). The polymerization using 4 equivalents of FeCl$_3$ versus monomer 1 also led to a higher polymer yield (40%, experiment 3, Table 7.3). However, the polymerization of 1,5-bis(phenylthio)pentane (2) (experiment 4, Table 7.3) under identical reaction conditions to those of 1,5-bis(phenoxypentane (1) (experiment 1, Table 7.3) produced a polymer yield of only 10%. This result suggests that the polymerizability of monomer 2 is lower than that of monomer 1. The polymer yields are also improved by the addition of a higher amount of FeCl$_3$ oxidant (experiments 5 and 6 Table 7.3).
Scheme 7.2. The cation-radical polymerization of 1,5-bis(phenoxypentane (1), its substituted derivatives (3-11), and 1,5-bis(phenylthio)pentane (2) monomers.
Table 7.3. Synthesis of Polyethers from 1,5-Bis(Phenoxy)Pentane (1) and 1,5-Bis(Phenylthio)Pentane (2)

<table>
<thead>
<tr>
<th>Exp. No.</th>
<th>Monomer/mmol</th>
<th>PhNO₂ (mL)</th>
<th>FeCl₃ (mmol)</th>
<th>PhNO₂ (mL)</th>
<th>Reaction Temperature (°C)</th>
<th>Reaction Time (h)</th>
<th>Polymer Yield (%)</th>
</tr>
</thead>
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<td>1.0</td>
<td>4.0</td>
<td>2.0</td>
<td>25</td>
<td>6</td>
<td>29&lt;sup&gt;a&lt;/sup&gt;</td>
</tr>
<tr>
<td>2</td>
<td>1/2.0</td>
<td>1.0</td>
<td>4.0</td>
<td>2.0</td>
<td>60</td>
<td>6</td>
<td>36&lt;sup&gt;a&lt;/sup&gt;</td>
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<tr>
<td>3</td>
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<td>8.0</td>
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<td>25</td>
<td>6</td>
<td>40&lt;sup&gt;a&lt;/sup&gt;</td>
</tr>
<tr>
<td>4</td>
<td>2/2.0</td>
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<td>4.0</td>
<td>2.0</td>
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<td>5.0</td>
<td>25</td>
<td>4</td>
<td>60&lt;sup&gt;a&lt;/sup&gt;</td>
</tr>
</tbody>
</table>

<sup>a</sup> Polymer is insoluble in chloroform, tetrahydrofuran, pyridine, N, N-dimethylformamide, dimethyl sulfoxide, and N-methylpyrrolidinone.
Both monomers 1 and 2 are soluble in nitrobenzene. However, as the polymerization progresses the resulting polymer precipitates from solution. The polymer isolated after the polymerization is insoluble in chloroform, tetrahydrofuran, dimethyl sulfoxide, N,N-dimethylformamide and N-methylpyrrolidinone. The insolubility of the polymers resulted from both 1 and 2 is most probably due to the biphenylene structural units in the polymers (eq 3, Scheme 7.2). The precipitation of the polymers from solution limits their molecular weights. Unfortunately, the resulting polymers can not be characterized by conventional solution techniques.

A series of monomers with the phenoxy rings of 1 substituted with various electron-donating groups like for example methyl, tert-butyl and methoxy groups were synthesized. The polymerization of these monomers is expected to produce a homogeneous reaction mixture since the resulting polymers are expected to be soluble.

The results of the polymerization of methyl substituted monomers are listed as experiments 1-6 from Table 7.4. Attempts to polymerize 1,5-bis(2,6-dimethylphenoxy)pentane (3) both at room temperature (experiment 1, Table 7.4) and at 60°C (experiment 2, Table 7.4) did not produce any polymer. The polymerization of 1,5-bis(3,5-dimethylphenoxy)pentane (4) led to a 13% polymer yield (experiment 3, Table 7.4). The resulting polymer has a number average molecular weight (Mn) of 5000 g/mol, with a polydispersity greater than 10.

The polymer resulted from 4 is soluble in chloroform and tetrahydrofuran. The structure of the polymer was determined by 200 MHz ¹H-NMR spectroscopy. A representative ¹H-NMR spectrum (CDCl₃, δ) is presented in Figure 7.1. The resonance of 3,5-dimethyl groups (protons B) is observed at 2.27 ppm. Each
Table 7.4. Synthesis of Polyethers from 1,5-Bis(Phenoxy)Pentane Derivatives (Monomers 3-11 in Table 7.1).

<table>
<thead>
<tr>
<th>Exp. No.</th>
<th>Monomer/mmol</th>
<th>PhNO₂ (mL)</th>
<th>FeCl₃ (mmol)</th>
<th>PhNO₂ (mL)</th>
<th>Reaction Temperature (°C)</th>
<th>Reaction Time (h)</th>
<th>Polymer Yield (%)</th>
<th>( \overline{M_n} ) (g/mol)</th>
<th>( \overline{M_w}/\overline{M_n} )</th>
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<td>6</td>
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<td>25</td>
<td>16</td>
<td>0</td>
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Figure 7.1. 200 MHz $^1$H-NMR spectrum (CDCl$_3$) of polymer derived from 1,5-bis(3,5-dimethylphenoxy)pentane (4) (Sample No. 3, Table 7.4).
repeating structural unit of the polymer should contain 12 such protons. However, the integral of the methyl group (2.27 ppm) is much lower than that of protons A (1.56-1.91 ppm) which correspond to only 6 protons for each repeating unit. Additional resonances were observed at 2.66, 3.51 and 4.50 ppm. These resonances are not expected from the polymer which should be resulted from the polymerization (eq 2, Scheme 7.2). By correlating the chemical shifts with the possible structure the resonances at 2.66, 3.51 and 4.50 are assigned respectively to 1,2-diphenylethane (protons C), diphenylmethane (protons D), and to benzyl chloride (protons F) groups. These structures are resulted from the proton transfer of the benzylic protons of the phenyl cation-radical to generate benzyl radicals which undergo subsequent reactions.

The polymerization of 1,5-bis(2,3-dimethylphenoxy)pentane (5) and 1,5-bis(2,3,5-trimethylphenoxy)pentane (6) led to 12 to 16% polymer yields. The polymers have $M_n$'s of 5800 and 7500 g/mol. The 200 MHz $^1$H-NMR spectra of these polymers resulting from both 5 and 6 have also 1,2-diphenylethane, diphenylmethane and benzyl chloride structure.

Scheme 7.3 presents the mechanism which accounts for the generation of the structures resulting from benzylic proton transfer. The structure of the methyl substituted monomers (4, 5, and 6) is represented as 12 in eq 4 from Scheme 7.3. The single electron transfer oxidation of the monomer 12 yields its corresponding cation-radical 13 (eq 4). Due to the strong electron-donating capability of the pentoxy group, the cation-radical 13 is stabilized by the oxonium cation-radical 14 (eq 5). The oxonium ion 14 is very stable and therefore unreactive. From the cation-radicals 13 and 14, 13 is relatively more reactive towards nucleophiles. However, the concentration of 13 is low since the equilibrium between 13 and 14
Scheme 7.3. The mechanism for the proton transfer reactions during the cation-radical polymerization of methyl substituted 1,5-bis(phenoxo)pentane monomers (4, 5 and 6).
is expected to be shifted towards 14 (eq 5). The elimination of a proton from both cation-radicals 13 and 14 leads to the benzylic radical 15 (eqs 6 and 7). Even though the oxonium cation-radical 14 is incapable of reacting with weak nucleophiles such as phenoxy groups, there is a possibility that it may be reactive to form a benzylic radical 15 by eq 7. Besides the reaction by eq 7 the oxonium cation-radical 14 just behaves like a reservoir to provide a low concentration of cation-radical 13 by eq 5.

The 1,2-diphenylethane 16 is generated by the radical-radical coupling of two benzylic radicals 15 (eq 8). The radical-radical coupling of benzylic radical 15 and of the cation-radical 13 followed by proton elimination leads to the diphenylmethane structure (17) (eq 9). The single electron transfer of the benzylic radical 15 forms its corresponding benzylic cation 18, which subsequently combines with the chloride anion most probably from the FeCl₄⁻ counter-anion leading to the benzyl chloride structure 19 (eq 10). Alternatively, the diphenylmethane structure 17 can also be generated by the electrophilic attack of the benzylic cation 18 on monomer 12 followed by proton release (eq 11).

The expected cation-radical polymerization⁷,⁸ proceeds by eq 12 from Scheme 7.4. In this reaction the cation-radical 13 attacks the neutral phenoxy ring of monomer 12 or the phenoxy chain end of the polymer (eq 12). A dimeric cation-radical 20 is generated. The single electron transfer between a dimeric cation-radical 20 and monomeric cation-radical 13 leads to a dimeric dication 21 (eq 13). 21 can also be formed by the alternative oxidation of dimeric cation-radical 20 by FeCl₃ oxidant (eq 14). The elimination of two protons yields a biphenyl structure 22 (eq 15).

From the ¹H-NMR spectrum of polymer derived from methyl substituted
Scheme 7.4. The cation-radical polymerization mechanism.
monomers (for example Figure 7.1 for polymer from 1,5-bis(3,5-dimethylphenoxy)pentane), it seems that the structure resulted from the aromatic-aromatic coupling (protons B) of the methyl substituted phenoxy groups is less than the structure generated by proton transfer generated reactions (protons C, D, and F). Therefore, the proton transfer of the methyl substituted monomers (4, 5, and 6) represents the main reaction during the cation-radical polymerization process. This is an expected result if we consider the low concentration of the cation-radical 13 and the presence of the oxonium cation-radical 14 (Scheme 7.3). The extensive proton transfer is believed to be facilitated by the relatively long lifetime of the stable oxonium cation-radical 14. During its lifetime, the oxonium cation-radical 14 undergoes only the observed proton transfer reactions.

The polymerization of 1,5-bis(2-tert-butylphenoxy)pentane (7), 1,5-bis(3-tert-butylphenoxy)pentane (8), and 1,5-bis(3,5-di-tert-butylphenoxy)pentane (9) led to low polymer yields (<10%) (experiments 6-9, Table 7.4). These polymerizations are retarded by the steric hindrance of the bulky tert-butyl groups. A representative 200 MHz ¹H-NMR spectrum of the polymer resulted from 9 is presented in Figure 7.2. In contrast to the polymers resulted from the methyl substituted monomers (Figure 7.1), the ¹H-NMR spectrum of the polymers from the tert-butyl substituted monomers does not exhibit any additional structure than the expected structure generated by cation-radical dimerization reaction (eq 2, Scheme 7.2). This is due to the absence of the benzylic protons in the monomer 9.

The polymerization of 1,5-bis(3-methoxyphenoxy)pentane (10) resulted in a 30% polymer yield (experiment 10, Table 7.4). The 200 MHz ¹H-NMR spectrum of a representative polymer obtained from 10 is presented in Figure 7.3. The structure of the polymer agrees with the expected structure (eq 2, Scheme 7.2).
Figure 7.2. 200 MHz $^1$H-NMR spectrum (CDCl$_3$) of polymer derived from 1,5-(3,5-di-tert-butylphenoxy)pentane (9) (Sample No. 9, Table 7.4).
Figure 7.3. 200 MHz $^1$H-NMR spectrum (CDCl$_3$) of polymer derived from 1,5-bis(3-methoxyphenoxy)pentane (10) (Sample No. 10, Table 7.4).
The polymerization of 1,5-bis(2,6-dimethylphenoxy)pentane (11) did not yield polymer (experiment 11, Table 7.4).

In order to understand the factors that determine the overall polymerizability of a monomer, the comparison between the 1,5-bis(phenoxy)pentanes and 4,4'-bis(phenoxy)diphenyl sulfones (Chapter 6) is presented in Scheme 7.5. The reactivity of a monomer affects the polymerizability in two steps, i.e. the oxidation of the monomer to its cation-radical (eq 4, Scheme 7.3) and the radical-substrate coupling (eq 12, Scheme 7.4). The oxidizability and the nucleophilicity of the monomer determine the reactivity of the monomer in these two steps respectively. Since the pentoxy group in monomer 1-11 (structure 23 from Scheme 7.5) is more electron-donating than the 4-sulfonylphenoxy group in monomer 26, monomer 23 is more reactive than monomer 26. However, the reactivity of the corresponding cation-radicals follows the opposite trend. Cation-radical 24 is stabilized by its oxonium cation-radical 25 (eq 10) and is less reactive than the cation-radical 27 since the cation in 27 can only be stabilized partially by the sulfonyl group of 28.

The insoluble nature of the polymers resulted from the unsubstituted monomers 1 and 2 does not allow a rigorous discussion on their polymerizability based on the heterogeneous polymerization results, which has the effects of the solubility of the polymers. The polymerizability of soluble monomers in Chapter 6 and in this chapter suggests that monomers containing the diphenyl sulfone linkage has higher polymerizability than the pentoxy linkage. This accordingly would indicate that the relative polymerizability between these two classes of monomers is determined by the reactivity of the cation-radical growing species. This implies that the difference between the reactivities of the cation-radicals of these two classes of monomers is larger than the difference between the reactivities of the corresponding
Scheme 7.5. A comparison of the polymerizability of the 1,5-bis-substituted pentane monomers and 4,4'-bis-substituted diphenyl sulfone monomers.
monomers.

7.4. CONCLUSIONS

The cation-radical resulted from the 1,5-bis(phenoxy)pentane (1), its substituted derivatives (3-11) and 1,5-bis(phenylthio)pentane (2) is stabilized by the corresponding oxonium or sulfonium cation-radical form. The stabilization reduces the reactivity of the cation-radicals by propagation through the non-oxonium or non-sulfonium cation-radicals. The stabilization further increases the lifetime of the cation-radicals which leads to the proton transfer for the methyl substituted monomers. The polymerizability of monomers 1-11 is relatively lower than that of the corresponding 4,4'-disubstituted diphenyl sulfone monomers. The relative polymerizability of these two classes of monomers seems to be determined by the reactivity of the cation-radical species.

REFERENCES

CHAPTER 8

ON THE POLYMERIZABILITY OF
4,4'-BIS(1-NAPHTHOXY)DIPHENYL SULFONE AND
1,5-BIS(1-NAPHTHOXY)PENTANE
IN THE CATION-RADICAL POLYMERIZATIONS

8.1. INTRODUCTION

Recently a novel method for the synthesis of aromatic polyether sulfones and polyether ketones was developed.\textsuperscript{1,2} It consists of the dehydrogenative crosscoupling polymerization of aromatic ether sulfone and ether ketone monomers through an oxidative polymerization reaction (Scholl reaction).\textsuperscript{3,4} The monomers investigated so far include, 4,4'-bis(1-naphthoxy)diphenyl sulfone,\textsuperscript{1} 4,4'-bis(1-naphthoxy)benzophenone,\textsuperscript{1} 4,4'-bis(phenoxyl)diphenyl sulfone,\textsuperscript{2} 4,4'-bis(phenylthio)diphenyl sulfone,\textsuperscript{2} and 4,4'-bis(phenoxyl)diphenyl sulfone substituted with a variety of electron-donating substituents.\textsuperscript{2} Monomers of different structures have revealed distinct reactivity during this polymerization. A cation-radical mechanism\textsuperscript{1,2} was proposed for this polymerization. The control of this polymerization reaction requires information about the reactivity of monomers and growing species of various structure, and on the overall polymerizability of the monomers. This information is not available since most of the polymerizations reported so far were performed under different experimental conditions.\textsuperscript{1,5}

This chapter describes a series of cation-radical polymerization experiments designed to provide information on the relative polymerizability of 4,4'-bis(1-naphthoxy)diphenyl sulfone and 1,5-bis(1-naphthoxy)pentane. The results are
important for both the design the structure of the monomers and for the understanding of the mechanism of the polymerizations.

8.2. EXPERIMENTAL

8.2.1. Materials

4,4'-Bis(1-naphthoxy)diphenyl sulfone\textsuperscript{1} (1) and 1,5-bis(1-naphthoxy)pentane\textsuperscript{5} (2) were synthesized as described. Anhydrous FeCl\textsubscript{3} (Aldrich) was used as received. Nitrobenzene (Fisher) was distilled from CaH\textsubscript{2}.

8.2.2. Polymerization Reactions

Polymerization of 4,4'-Bis(1-naphthoxy)diphenyl Sulfone and of 1,5-Bis(1-Naphthoxy)pentane

The polymerization procedure used in all experiments was identical to that previously described.\textsuperscript{1,2} Detailed experimental conditions are listed in Table 8.1. The total polymer yield is based on the overall weight of the polymer separated by precipitation into methanol, followed by washing with boiling methanol. The polymer was then dissolved in boiling CHCl\textsubscript{3}, and the insoluble fraction was separated by filtration to yield the gel fraction. The chloroform solution was then precipitated into methanol, and the reprecipitated polymer yielded the soluble polymer fraction.

8.3. RESULTS AND DISCUSSION

The oxidative polymerizations of 4,4'-bis(1-naphthoxy)diphenyl sulfone (1) and 1,5-bis(1-naphthoxy)diphenyl sulfone (2) are outlined in Scheme 8.1. Both polymerizations were performed under a N\textsubscript{2} atmosphere in dry nitrobenzene
Table 8.1. Influence of Polymerization time on the Polymerization of 4,4'-Bis(1-Naphthoxy)Diphenyl Sulfone (1) and 1,5-Bis(1-Naphthoxy)Pentane (2). Polymerization Temperature, 25°C.

<table>
<thead>
<tr>
<th>Exp. No.</th>
<th>Monomer Solution</th>
<th>FeCl₃ Solution</th>
<th>PhNO₂ Reaction Time (h)</th>
<th>Total Polymer Yield (%)</th>
<th>Gel Yield (%)</th>
<th>Soluble Polymer Fraction Yield (%)</th>
<th>Mn (g/mol)</th>
<th>Mw/Mn</th>
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<td>4.0</td>
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<td>0.5</td>
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<td>5.8</td>
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<tr>
<td>2</td>
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<td>4.0</td>
<td>2.5</td>
<td>1.0</td>
<td>98.1</td>
<td>6.2</td>
<td>91.9</td>
</tr>
<tr>
<td>3</td>
<td>1/1.0</td>
<td>1.0</td>
<td>4.0</td>
<td>2.5</td>
<td>2.0</td>
<td>98.7</td>
<td>18.5</td>
<td>80.2</td>
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<tr>
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<td>1.0</td>
<td>4.0</td>
<td>2.5</td>
<td>4.0</td>
<td>98.9</td>
<td>19.0</td>
<td>79.9</td>
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<td>4.0</td>
<td>2.5</td>
<td>0.5</td>
<td>58.2</td>
<td>3.2</td>
<td>55.0</td>
</tr>
<tr>
<td>6</td>
<td>2/1.0</td>
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<td>4.0</td>
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<td>1.0</td>
<td>84.1</td>
<td>3.6</td>
<td>80.5</td>
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<td>4.0</td>
<td>2.5</td>
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<td>90.0</td>
<td>4.4</td>
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<td>4.0</td>
<td>2.5</td>
<td>4.0</td>
<td>90.2</td>
<td>5.3</td>
<td>84.9</td>
</tr>
</tbody>
</table>
Scheme 8.1. The oxidative polymerization of 4,4'-bis(1-naphthoxy)diphenyl sulfone (1) and 1,5-bis(1-naphthoxy)pentane (2).
using FeCl₃ as oxidant. The polymerization of 1 and 2 leads to polymers 3 and 4 respectively. In this study, the molar concentrations of both monomers and anhydrous FeCl₃ were maintained constant. The polymerization experiments were performed at four different reaction times, i.e. 0.5, 1.0, 2.0, and 4.0 h respectively. The [FeCl₃]/[Monomer] molar ratio was maintained equal to 4/1. The experimental conditions and the polymerization results are listed in Table 8.1.

In all polymerization experiments, an insoluble polymer fraction was obtained. The total polymer yield, which includes the gel and the soluble fractions, is plotted in Figure 8.1 as a function of polymerization time. Curves A and B represent the total polymer yield derived from monomers 1 and 2, respectively. For both monomers 1 and 2, the total polymer yield increases with increasing polymerization time. However, the yield of the polymer 3 which is derived from monomer 1 reaches 96.0% within a very short reaction time (about 0.5 h) and then over the rest of the polymerization time (about 3.5 h) increases only from 96.0% to 98.9%. In contrast, the yield of the polymer 4 derived from the monomer 2 increases from 58.2% to 90.2% during 4 h reaction time. It is also important to note that at equal reaction times the yield of polymer 3 is always higher than that of the polymer 4. These results demonstrate that the rate of polymerization of 1 is consistently higher than that of 2. Therefore, under these polymerization conditions, the polymerizability of 4,4-bis(1-naphthoxy)diphenyl sulfone (1) is higher than that of 1,5-bis(1-naphthoxy)pentane (2).

The dependences of the polymer molecular weight of the soluble fraction versus the polymerization time are plotted in Figure 8.2. Curves A and B show the dependence of $\overline{M}_n$ on the polymerization time for monomers 1 and 2, respectively. Both curves have a maximum of $\overline{M}_n$ at intermediary reaction times. At reaction
Figure 8.1. The dependence of total polymer yield on the polymerization time: A) polymerization of 4,4'-bis(1-naphthoxy)diphenyl sulfone; B) polymerization of 1,5-bis(1-naphthoxy)pentane.
Figure 8.2. The dependence of number average molecular weight ($M_n$) of soluble polymer fraction on the polymerization time: A) polymerization of 4,4'-bis(1-naphthoxy)diphenyl sulfone; B) polymerization of 1,5-bis(1-naphthoxy)pentane.
times shorter than 1 h Curve B is higher than curve A. This trend reverses for reaction times longer than 2 h. This complicated molecular weight dependence on reaction time requires a quantitative analysis of the amount of the polymer gel at each polymerization time.

Figure 8.3 shows the yield of the polymer gel as a function of polymerization time. Curves A and B represent the amount of gel separated from the polymerization of 1 and 2 respectively. Curve A is much higher than Curve B at all polymerization times. Curve A also shows a sharp increase in the gel yield between 1 and 2 h. In contrast, Curve B increases only slightly as the reaction time increases. The higher initial gel content formed during the polymerization of 1 results in a lower \( M_n \) of the soluble fraction, since some of the high molecular weight fraction has already been transformed into the crosslinked insoluble polymer fraction. As the polymerization proceeds, the monomer concentration decreases and the polymer is first branched and subsequently crosslinked by the reaction of the reactive growing chain on the polymer backbone units. This effect determines that the \( M_n \) of soluble fraction will decrease after reaching a maximum. This maximum corresponds to the branched polymer before the gel point. In fact, this trend has been experimentally observed as shown in Figure 8.2.

The dependence of the amount of soluble polymer fraction on the polymerization time is presented in Figure 8.4. Curves A and B refer to the soluble fractions of polymer 3 and polymer 4 respectively. Curve B increases dramatically as the reaction time varies from 0.5 to 2 h. A slight decrease follows afterwards. Curve A increases slightly between 0.5 and 2 h, followed by a drop of about 10% in the polymer yield. These variations are accordingly caused by the different
Figure 8.3. The dependence of the yield of the polymer gel on the polymerization time: A) polymerization of 4,4'-bis(1-naphthoxy)diphenyl sulfone; B) polymerization of 1,5-bis(1-naphthoxy)pentane.
Figure 8.4. The dependence of the yield of the soluble polymer fraction on the polymerization time: A) polymerization of 4,4'-bis(1-naphthoxy)diphenyl sulfone; B) polymerization of 1,5-bis(1-naphthoxy)pentane.
amount of polymer gel formed (Figure 8.3).

The $M_n$ of the soluble fraction is plotted as a function of the total polymer yield in Figure 8.5. Curves A and B refer to the $M_n$ of polymer 3 and polymer 4 respectively. Curve A is covering only the range of the total polymer yields higher than 96.0%. This curve has a maximum on the $M_n$-Polymer Yield plot. Curve B also reaches a maximum. These trends are expected from the $M_n$ versus polymerization time plot (Figure 8.2), and are caused by the formation of polymer gel.

Although only in a relative way, both the $M_n$ of the soluble polymer fraction and the yields of the overall, soluble and insoluble polymer fractions provide a reasonable estimate of the polymerizability of these two monomers. They suggest that the rate of the polymerization of 4,4'-bis(1-naphthoxy)diphenyl sulfone (1) is higher than that of 1,5-bis(1-naphthoxy)pentane (2).

A reasonable explanation for the observed difference between the polymerizability of these two monomers requires a brief discussion of the influence of molecular structure on the reactivities of both monomers and their corresponding growing species. Scheme 8.2 provides a parallel consideration of both monomers during this polymerization. The first step in the polymerization of 1 represents the oxidation of 1 to generate the cation-radical intermediate 5 (eq 2, Scheme 8.2). The cation-radical 5 has two options. First, 5 functions as an electrophile and therefore attack the monomer 1 with the formation of 7, followed by a proton release, further oxidation, etc., to generate the linear polymer 3 (eq 3). Secondly, 5 may react with an internal 1,1'-binaphthyl unit 8 at the highest electron density position, i.e., C-2, leading to the intermediate 9. The subsequent reactions of 9 first form a branched and then a crosslinked polymer 3.
Figure 8.5. The dependence of number average molecular weight ($\bar{M}_n$) of the soluble polymer fraction on the overall polymer yield: A) polymerization of 4,4'-bis(1-naphthoxy)diphenyl sulfone; B) polymerization of 1,5-bis(1-naphthoxy)pentane.
Scheme 8.2. The cation-radical polymerization mechanism of 4,4'-bis(1-naphthoxy)diphenyl sulfone (1) and 1,5-bis(1-naphthoxy)pentane (2).
The corresponding reactions of monomer 2 are shown in eqs 5-7 from Scheme 8.2. The difference between the polymerizability of monomers 1 and 2 is determined by the difference between the reactivities of the monomers and of the corresponding cation-radical growing species 5 and 10. Monomer 2 is more reactive than monomer 1, because the presence of an alkoxy group in monomer 2 makes its oxidation potential be lower than that of monomer 1. The cation charge on the 1-naphthoxy ring in 5 derived from monomer 1 can only be partially delocalized onto the sulfonylephenoxy group as shown in the resonance structure 6 (eq 2). In contrast, the cation charge in the corresponding cation-radical 10 derived from monomer 2 can be completely delocalized on the alkoxy oxygen to form the oxonium species 11 (eq 5), which is unreactive. The radical of the resonance structure 11 is unreactive in radical-radical coupling reactions, because the radical is resonance stabilized due to its location at both allylic and benzylic position. Also the radical is located on a six-membered ring which is sterically unfavorable for radical-radical coupling reactions\(^2\).

The comparison of the growing species 5 and 10 indicates that 10 is more delocalized and thus more stable or unreactive than 5. The rate of the propagation reactions (eqs 3 and 6) are determined by both the reactivity or the nucleophilicity of the monomers and by the reactivity of the growing cation-radical species. The nucleophilicity of monomer 2 is higher than that of monomer 1, while the reactivity of the cation-radical derived from monomer 1 is higher than that of monomer 2. The experimental results have shown consistently higher overall polymer yield for the polymerization of monomer 1 (Figure 8.1) and also higher maximum \(M_n\) (Figure 8.2). Therefore the polymerizability of these monomers is predominantly
determined by the reactivity of the growing species. This leads to a higher polymerizability of monomer 1.

The difference between the polymerizability of the two monomers is determined by both the reactivity of the monomers and of their corresponding growing species. However, which of the reactivities dominates the polymerizability is determined by the relative differences between the reactivities of monomers and of the growing species. In the present case, the difference between the reactivity of the growing species is a dominant factor since the difference between the reactivity of the growing species is larger than that between the reactivity of the monomers. However, for the polymerization of 4,4'-bis(1-phenoxy)diphenyl sulfone and 4,4'-bis(1-phenylthio)diphenyl sulfone, the reactivity of the monomer determines the overall polymerizability since the difference between the reactivity of the growing species is smaller than that between the reactivity of the monomers.

The difference between the polymer gel content reflects the selectivity of the respective growing species. The growing species 5 derived from monomer 1 has higher reactivity than that of 10 derived from monomer 2. Therefore, the cation-radical 5 should have a lower selectivity than the cation-radical 10. The monomers 1 and 2 and the chain ends of their polymers are more nucleophilic than the internal 1,1'-binaphthyl unit from 8 or 13. This is due to the presence of the 4-position of the naphthalene unit, which has the highest electron density, in both monomers 1, 2, and at the chain ends of a polymer molecule. The 4-position of the naphthalene unit is not available in compounds 8 and 13 and therefore, decreases the probability of these reactions. The 2-positions in structures 8 and 13 are also sterically hindered by the 1-phenoxy group (in 8) or 1-alkoxy group (in 13) by
comparison with the 4-positions from the monomers 1 and 2 and from the chain ends of the corresponding polymers. These two factors determine that the formation of linear polymers is kinetically favored versus the generation of branched and subsequently crosslinked polymer fractions. The polymerization of monomer 1 has produced higher contents of polymer gel than that resulted from the polymerization of monomer 2. This demonstrates that the growing species 5 derived from monomer 1 is less selective than that of 10 derived from monomer 2. The experimental observation of polymer gel content also suggests that the growing species 5 is more reactive than the growing species 10.

8.4. CONCLUSIONS

Under identical experimental conditions, the polymerization of 4,4'-bis(1-naphthoxy)diphenyl sulfone (1) produced polymers of higher overall yield and higher number average molecular weight ($M_n$) than those resulted from the polymerization of 1,5-bis(1-naphthoxy)pentane (2). The polymerizability of monomer 1 is higher than that of monomer 2. This behavior is predominantly due to the higher reactivity of the radical-cation growing species derived from monomer 1. The polymer gel content is determined by the selectivity of the growing species. The consistently higher polymer gel content obtained during the polymerization of monomer 1 also suggests that the radical-cation growing species derived from monomer 1 are more reactive than those derived from monomer 2.
REFERENCES


CHAPTER 9

HOMOPOLYMERIZATION AND COPOLYMERIZATION OF $\alpha,\omega$-BIS[4-(1-NAPHTHOXY)PHENYL]-PERFLUROALKANES

9.1. INTRODUCTION

Polyether sulfones are frequently synthesized by the aromatic nucleophilic substitution of 4,4'-dihaloaromatic sulfones by bisphenolate nucleophiles, and by aromatic electrophilic sulfonylation.\textsuperscript{1,2} Two novel approaches to the synthesis of polyether sulfones were recently reported. The first one consists of the Scholl reaction\textsuperscript{3-7} of 4,4'-bis(1-naphthoxy)diphenyl sulfone.\textsuperscript{8} The formation of C-C aromatic bonds during this polymerization process is assumed to occur through a cation-radical mechanism. The second method consists of a Ni\textsuperscript{0} catalyzed crosscoupling of 4,4'-bis(p-chlorophenoxy)diphenyl sulfone.\textsuperscript{9}

Highly fluorinated polymers exhibit high toughness, flexibility, excellent cryogenic properties,\textsuperscript{10} nonadhesiveness and low coefficients of frictions.\textsuperscript{11} These properties are mostly determined by the extremely low surface free energy of fluorinated polymers. Therefore, it is of particular interest to incorporate these unusual properties into polyether sulfone polymers. A series of polyether sulfones containing perfluoroalkyl moieties have been recently prepared by aromatic nucleophilic substitution.\textsuperscript{12}

The first goal of this chapter is to describe the synthesis of the first examples of polyether sulfones containing both perfluoroalkyl and 1,1'-binaphthyl ether structural units by a room temperature Scholl reaction. The second objective is to
elucidate the effect of the perfluoroalkylsulfonyl group on the polymerizability of the monomers and of the corresponding cation-radical growing species by copolymerization experiments.

9.2. EXPERIMENTAL

9.2.1. Materials

4-Fluorothiophenol (Aldrich, 99%), sodium carbonate (Fisher), and anhydrous ferric chloride (Aldrich, >98%) were used as received. Nitrobenzene was distilled from calcium hydride under vacuum. N,N-Dimethylacetamide (DMAc) was distilled under argon at atmospheric pressure and stored under argon. 4,4’-Bis(1-naphthoxy)diphenyl sulfone and 1,5-bis(1-naphthoxy)pentane were synthesized as reported previously.7,8 All the other reagents were used as received or purified by standard procedures.

9.2.2. Special Techniques

Gel permeation chromatography (GPC) measurements of the homopolymers 2a and 2b were carried out on a Waters instrument equipped with a Waters 510 pump, a Waters 484 variable wavelength UV detector, and a Maxima 820 data station. The analyses were made using THF as solvent (1 mL/min, 40°C), a set of PL-gel columns of 5 x 10^2, 10^3, and 10^4 Å, and a calibration plot constructed with polystyrene standards. The GPC analyses of the copolymers were performed on a Perkin-Elmer series 10LC instrument equipped with an LC-100 column oven, an LC 600 autosampler, and a Nelson Analytical data station. The measurements were made using a UV detector set at 254 nm, chloroform as solvent (1mL/min, 40°C), a set of PL-Gel columns of 5 x 10^2 and 10^4 Å, and a calibration plot constructed with
polystyrene standards (Supelco). A Perkin-Elmer DSC-4 differential scanning calorimeter, equipped with a TADS 3600 data station, was used to determine the glass transition temperatures of the polymers at a heating rate of 20°C/min. The glass transition temperature was read at the middle of the change in the heat capacity. Thermogravimetric analyses (TGA) were carried out on a Shimazu thermal analyzer TGA-40M at a heating rate of 10°C/min.

9.2.3. Synthesis of the Monomers

The synthesis of monomers containing perfluoroalkylsulfonyl groups is outlined in Scheme 9.1.

Synthesis of 1,4-Bis[4-(1-naphthoxy)phenylsulfonyl]perfluorobutane (1a)

A mixture of 1-naphthol (11.5 g, 0.08 mol), 1,4-bis(4-fluorophenylsulfonyl)perfluorobutane\textsuperscript{12} (18.4 g, 0.036 mol), and sodium carbonate (12.7 g, 0.12 mol) in 100 mL of DMAc was stirred under argon for 0.5 h at 25°C, 3 h at 45°C and 3 h at 60°C. The resulting mixture was poured into water and extracted with ether. The ether extracts were washed with 10% aqueous sodium carbonate and water, dried over MgSO\textsubscript{4} and concentrated on a rotary evaporator. The residue was recrystallized, first from ethyl acetate/hexane and then from benzene using Darco\textsuperscript{®} to give 22.6 g (82%) of product, mp 219-219.5°C. \textsuperscript{1}H-NMR (\textdelta, ppm, CDCl\textsubscript{3}): 7.12 (d, 4H, meta SO\textsubscript{2}-Ar-H), 7.24 (t, 2H, 2-H on the naphthalene unit), 7.53 (m, 6H, 3-, 6-, and 7-H's on the naphthalene unit), 7.81 (d, 2H, 4-H on the naphthalene unit), 7.91 (d, 4H, ortho SO\textsubscript{2}-Ar-H), 7.96 (d, 4H, 5- and 8-H's on the naphthalene unit). \textsuperscript{19}F-NMR (\textdelta, ppm, CDCl\textsubscript{3}): -110.4 (4F), -
118.6 (4F). Anal. Calcd. for C_{36}H_{22}F_{8}S_{2}O_{6}: C, 56.39; H, 2.89; F, 19.82. Found: C, 56.90; H, 2.89; F, 19.73.

**Synthesis of 1,8-Bis[4-(1-naphthoxy)phenylsulfonyl]perfluorooctane (1b).**

A mixture of 1-naphthol (5.3 g, 0.037 mol), 1,8-bis(4-fluorophenylsulfonyl)perfluorooctane\(^{12}\) (10.8 g, 0.015 mol), and sodium carbonate (5.8 g, 0.054 mol) in 100 mL of DMAc was stirred under argon at 75°C for 8 h. The resulting mixture was poured into water and extracted with ether. The ether extracts were washed with 10% aqueous sodium carbonate and water, dried over MgSO\(_4\) and concentrated on a rotary evaporator. The residue was recrystallized twice from ethyl acetate/hexane to give 9.0 g (62%) of product, mp 134.5-135.5°C. \(^1\)H-NMR (δ, ppm, CDCl\(_3\)): 7.15 (d, 4H, meta SO\(_2\)-Ar-H), 7.23 (t, 2H, 2-H on the naphthalene unit), 7.53 (m, 6H, 3-, 6-, and 7-H's on the naphthalene unit), 7.83 (d, 2H, 4-H on the naphthalene unit), 7.91 (d, 4H, ortho SO\(_2\)-Ar-H), 7.95 (d, 4H, 5- and 8-H's on the naphthalene unit). \(^19\)F-NMR (δ, ppm, CD\(_2\)Cl\(_2\)): -111.8 (4F), -120.0 (4F), -121.7 (8F). Anal. Calcd. for C\(_{40}\)H\(_{22}\)F\(_{16}\)S\(_2\)O\(_6\): C, 49.70; H, 2.29; F, 31.44. Found: C, 49.39; H, 2.50; F, 31.84.

**9.2.4. Polymerization Reactions**

The polymerization reactions are outlined in Schemes 9.2-9.4.

**Homopolymerization of 1a and of 1b**

the homopolymerizations were performed with 1.00 g of monomer and 4 equivalents of anhydrous FeCl\(_3\) versus the number of moles of monomer. The homopolymerization conditions are listed in Table 9.1. A typical example is given
as follows. 1,8-Bis[4-(1-naphthoxy)phenylsulfonyl]perfluoroctane (1b) (1.000 g, 1.0 mmol) was dissolved in 2.5 mL nitrobenzene under nitrogen by stirring at 40-50°C. The mixture was cooled down to 25°C, to which a solution of anhydrous ferric chloride (0.630 g, 3.9 mmol) in 5.0 mL nitrobenzene was added dropwise over 40 min period under nitrogen. The reaction mixture was stirred for additional 30 min. The mixture was poured into 300 mL methanol acidified with 2% HCl. The precipitate was washed with hot methanol and dried in vacuo to yield 0.98 g (97%) polymer. The polymer was then dissolved in 15 mL chloroform and precipitated into 300 mL methanol. The precipitate was filtered and dried in vacuo to yield 0.72 g (75%) of polymer 2b. The inherent viscosity in chloroform measured at a concentration of 0.5 g/dL at 30°C was 0.71 dL/g, $\bar{M}_n$ (GPC) = 38,000 g/mol, $\bar{M}_w/\bar{M}_n$=2.8.

Copolymerization Experiments

All the copolymerization conditions are listed in Table 9.2. In a typical copolymerization experiment, 1,4-bis[4-(1-naphthoxy)phenylsulfonyl]perflurobutane (1a) (0.383 g, 0.5 mmol) and 4,4'-bis(1-naphthoxy)diphenyl sulfone (4) (0.251 g, 0.5 mmol) were dissolved in 2.5 mL dry nitrobenzene at 50°C under nitrogen. To the cooled reaction mixture, a solution of ferric chloride (0.650 g, 4 mmol) in 6.0 mL dry nitrobenzene was added dropwise over a period of 40 min. The reaction mixture was stirred under nitrogen for 3.0 h. The reaction mixture was precipitated into 400 mL methanol. The collected precipitate was dissolved in 20 mL chloroform, the chloroform solution was filtered to yield 0.001 g (0.2%) of insoluble polymer gel. The filtered chloroform solution was precipitated into 400 mL methanol acidified with 2% HCl. The precipitate was filtered and dried in
Scheme 9.3. Copolymerization of 1,4-bis[4-(1-naphthoxy)phenylsulfonyl]perfluorobutane (1a) and 1,8-bis[4-(1-naphthoxy)phenylsulfonyl]-perfluoroctane (1b).
Scheme 9.4. Copolymerization of \( \alpha, \omega \)-bis[4-(naphthoxy)phenylsulfonyl]-perfluoroalkanes with 4,4'-bis(1-naphthoxy)phenylsulfone (4) and 1,5-bis(1-naphthoxy)-pentane (5).
vacuo to yield 0.443 g (70.0%) of polymer \( \mathcal{M}_a \): \( \overline{M}_n \) (GPC) = 15,100 g/mol, \( \overline{M}_w/\overline{M}_n \) = 2.26.

9.3. RESULTS AND DISCUSSION

The \( \alpha,\omega \)-bis[4-(1-naphthoxy)phenylsulfonyl]perfluoralkane monomers 1a and 1b were prepared by an aromatic nucleophilic displacement reaction of \( \alpha,\omega \)-bis(4-fluorophenylsulfonyl)perfluoralkane\(^{12} \) and 1-naphthol. The synthesis is shown in Scheme 9.1.

The fluorinated polyethersulfones 2a and 2b are synthesized by the Scholl reaction as shown in Scheme 9.2. The polymerization consists of a room temperature reaction of the respective monomers dissolved in dry nitrobenzene in the presence of anhydrous ferric chloride. Polymerizations were performed under a stream of nitrogen. The mechanism of the Scholl reaction was assumed to proceed through a radical-cation intermediate derived from the single electron oxidation of the monomer, and its subsequent electrophilic addition to the nucleophilic monomer.\(^{6-8} \)

The results of the homopolymerization experiments are summarized in Table 9.1. These polymerizations were performed with a molar ratio of [FeCl\(_3\)]/[monomer] equal to 4/1, and with different monomer and FeCl\(_3\) concentrations at various reaction times. Polymer 2a was obtained with inherent viscosities ranging from 0.38 to 0.66 dL/g. However, polymerizations performed at high concentration of monomer and ferric chloride resulted in insoluble polymers, probably due to branching and subsequent crosslinking of the resulted polymers. Monomer 1b yielded polymer 2b of inherent viscosities in the range of 0.50 to 0.71 dL/g. GPC analyses performed with polystyrene standards on polymer 2a
Table 9.1. The Synthesis of Fluorinated Polyether Sulfones. Polymerization Temperature, 25 °C.

<table>
<thead>
<tr>
<th>Exp. No.</th>
<th>Monomer/mmol</th>
<th>PhNO₂ (mL)</th>
<th>FeCl₃ (mmol)</th>
<th>PhNO₂ (mL)</th>
<th>Reaction Time (h)</th>
<th>Polymer Yield (%)</th>
<th>Polymer/ηₐ (dL/g)</th>
<th>Mn (g/mol)</th>
<th>Mw/Mn</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>la/1.3</td>
<td>2.0</td>
<td>5.2</td>
<td>3.2</td>
<td>1.5</td>
<td>la/63b</td>
<td>0.55</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>2</td>
<td>la/1.3</td>
<td>2.0</td>
<td>5.2</td>
<td>3.2</td>
<td>3.5</td>
<td>la/95c</td>
<td>-</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>3</td>
<td>la/1.3</td>
<td>2.5</td>
<td>5.2</td>
<td>4.0</td>
<td>0.7</td>
<td>la/55b</td>
<td>0.66</td>
<td>33,000</td>
<td>2.3</td>
</tr>
<tr>
<td>4</td>
<td>la/1.3</td>
<td>2.5</td>
<td>4.9</td>
<td>4.0</td>
<td>3.0</td>
<td>la/96c</td>
<td>-</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>5</td>
<td>la/1.3</td>
<td>2.5</td>
<td>4.9</td>
<td>5.0</td>
<td>1.3</td>
<td>la/79b</td>
<td>0.53</td>
<td>-</td>
<td>-</td>
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<tr>
<td>6</td>
<td>la/1.3</td>
<td>2.5</td>
<td>4.9</td>
<td>6.0</td>
<td>3.3</td>
<td>la/83b</td>
<td>0.50</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>7</td>
<td>la/1.3</td>
<td>2.5</td>
<td>4.9</td>
<td>6.0</td>
<td>3.3</td>
<td>la/99c</td>
<td>-</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>8</td>
<td>la/1.3</td>
<td>3.0</td>
<td>4.9</td>
<td>7.0</td>
<td>3.0</td>
<td>la/70b</td>
<td>0.38</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>9</td>
<td>la/1.3</td>
<td>3.0</td>
<td>4.9</td>
<td>7.0</td>
<td>3.0</td>
<td>la/82d</td>
<td>-</td>
<td>17,500</td>
<td>3.6</td>
</tr>
<tr>
<td>10</td>
<td>lb/1.0</td>
<td>2.5</td>
<td>3.9</td>
<td>4.0</td>
<td>1.7</td>
<td>lb/45b</td>
<td>0.51</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>11</td>
<td>lb/1.0</td>
<td>2.5</td>
<td>3.9</td>
<td>5.0</td>
<td>1.2</td>
<td>lb/75b</td>
<td>0.71</td>
<td>38,000</td>
<td>2.8</td>
</tr>
<tr>
<td>12</td>
<td>lb/1.0</td>
<td>2.5</td>
<td>3.9</td>
<td>6.0</td>
<td>3.0</td>
<td>lb/50b</td>
<td>0.42</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>13</td>
<td>lb/1.0</td>
<td>2.5</td>
<td>3.9</td>
<td>6.0</td>
<td>4.7</td>
<td>lb/40b</td>
<td>0.50</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>14</td>
<td>lb/1.0</td>
<td>2.5</td>
<td>4.0</td>
<td>6.0</td>
<td>3.0</td>
<td>lb/92e</td>
<td>-</td>
<td>28,000</td>
<td>3.4</td>
</tr>
</tbody>
</table>

a) measured at a concentration of 0.5 g/dL in chloroform at 30°C.
b) measured after reprecipitation from chloroform solution into methanol.
c) insoluble polymer was obtained.
d) total polymer yield including 1% isolated polymer gel.
e) total polymer yield including 7% isolated polymer gel.
have demonstrated that \( \eta_{inh} = 0.66 \text{ dL/g} \) corresponds to \( \overline{M}_n = 33,000 \text{ g/mol} \), with a polydispersity \( (\overline{M}_w/\overline{M}_n) \) of 2.3. The GPC analyses of the polymer 2b with \( \eta_{inh} = 0.71 \text{ dL/g} \) provided \( \overline{M}_n = 38,000 \text{ g/mol} \), \( \overline{M}_w/\overline{M}_n = 2.8 \).

The 200 MHz \(^1\text{H}-\text{NMR} \) spectra of monomer 1a (Spectrum A) and its polymer 2a (Spectrum B) are presented in Figure 9.1. After polymerization the resonance of protons D disappears, while the resonances due to protons A, B, E and F were shifted downfield.

In order to obtain further information on the reactivity of these two fluorinated monomers, we performed a series of copolymerizations of monomers 1a, 1b, 4,4'-bis(1-naphthoxy)diphenyl sulfone (4) and 1,5-bis(1-naphthoxy)pentane (5). These copolymerization reactions are shown in Scheme 9.3 and Scheme 9.4. The copolymerization results are summarized in Table 9.2.

The copolymerization of fluorinated monomers 1a and 1b of different \((\text{CF}_2)_n\) spacer lengths (4 for 1a and 8 for 1b) is shown in Scheme 9.3. This copolymerization led to 85.4% soluble and 0.8% insoluble fractions of copolymer 3. The \( \overline{M}_n \) of this copolymer is 10,500 g/mol, with \( \overline{M}_w/\overline{M}_n = 2.94 \). The 200 MHz \(^1\text{H}-\text{NMR} \) spectrum of this copolymer is presented in Figure 9.2. This spectrum resembles the \(^1\text{H}-\text{NMR} \) spectrum of the homopolymer 2a derived from 1a (Spectrum B, Figure 9.1). This result is expected since no strong effect of the \((\text{CF}_2)_n\) spacer lengths on the reactivity of these two monomers and of their growing species should be expected. Also, the chemical shifts of the monomer units in the copolymer are not strongly affected by the \((\text{CF}_2)_n\) spacer lengths.

The copolymerization of either 1a or 1b with 4,4'-bis(1-naphthoxy)diphenyl sulfone (4) results in polymer yields of 70.0% and 90.8% respectively (Table 9.2). These copolymers have \( \overline{M}_n \) about 15,000 g/mol, and
Figure 9.1. 200 MHz $^1$H-NMR spectra of 1a (spectrum A) and polymer 2a (Sample No. 9, Table 9.1) derived from 1a (spectrum B) (an expansion of 6-9 ppm ($\delta$), in CDCl$_3$, TMS, 25 °C).
Table 9.2. The Synthesis of Fluorinated Polyether Sulfone Copolymers. Polymerization Temperature, 25 °C; Polymerization Time, 3.0 h.

<table>
<thead>
<tr>
<th>Exp. No.</th>
<th>Monomer 1 /mmol</th>
<th>Monomer 2 /mmol</th>
<th>PhNO₂ (mL)</th>
<th>FeCl₃ (mmol)</th>
<th>PhNO₂ (mL)</th>
<th>Copolymer/Total Polymer Yield (%)</th>
<th>Gel Yield (%)</th>
<th>Soluble Polymer</th>
<th>Yield (%)</th>
<th>Mn (g/mol)</th>
<th>Mw/Mn</th>
<th>Tg (°C)</th>
</tr>
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<tbody>
<tr>
<td>1</td>
<td>1a/0.5</td>
<td>1b/0.5</td>
<td>2.5</td>
<td>4.0</td>
<td>6.0</td>
<td>3/86.2</td>
<td>0.8</td>
<td>85.4</td>
<td>10,500</td>
<td>2.94</td>
<td>171</td>
<td></td>
</tr>
<tr>
<td>2</td>
<td>1a/0.5</td>
<td>4/0.5</td>
<td>2.5</td>
<td>4.0</td>
<td>6.0</td>
<td>6a/70.2</td>
<td>0.2</td>
<td>70.0</td>
<td>15,100</td>
<td>2.26</td>
<td>-</td>
<td></td>
</tr>
<tr>
<td>3</td>
<td>1a/0.5</td>
<td>5/0.5</td>
<td>2.5</td>
<td>4.0</td>
<td>6.0</td>
<td>7a/52.7</td>
<td>0</td>
<td>52.7</td>
<td>18,100</td>
<td>10.28*</td>
<td>-</td>
<td></td>
</tr>
<tr>
<td>4</td>
<td>1b/0.5</td>
<td>4/0.5</td>
<td>2.5</td>
<td>4.0</td>
<td>6.0</td>
<td>6b/91.0</td>
<td>0.2</td>
<td>90.8</td>
<td>15,000</td>
<td>2.71</td>
<td>200</td>
<td></td>
</tr>
<tr>
<td>5</td>
<td>1b/0.5</td>
<td>5/0.5</td>
<td>2.5</td>
<td>4.0</td>
<td>6.0</td>
<td>7b/50.0</td>
<td>0.2</td>
<td>49.8</td>
<td>10,400</td>
<td>8.38b</td>
<td>154</td>
<td></td>
</tr>
</tbody>
</table>

a) Bimodal molecular weight distribution was observed. The two peaks have peak $\overline{M}_n$ of 71,400 ($\overline{M}_w/\overline{M}_n=3.53$) and 4,800 ($\overline{M}_w/\overline{M}_n=1.25$), respectively.

b) Bimodal molecular weight distribution was observed. The two peaks have peak $\overline{M}_n$ of 44,000 ($\overline{M}_w/\overline{M}_n=3.02$) and 4,500 ($\overline{M}_w/\overline{M}_n=1.31$), respectively.
Figure 9.2. 200 MHz $^1$H-NMR spectrum of copolymer 3 (Sample No. 1, Table 9.2) derived from 1a and 1b (an expansion of 6-9 ppm (δ), in CDCl$_3$, TMS, 25 °C).
$\overline{M}_w/\overline{M}_n$ of 2.26 and 2.71.

200 MHz $^1$H-NMR spectrum of copolymer 6a derived from 1a and 4 is shown in Figure 9.3. However, direct determination of the copolymer composition is not possible by $^1$H-NMR spectroscopy due to the overlap of the respective resonances.

Typical GPC traces of representative homopolymer 2b, and copolymers 3 and 6a are presented in Figure 9.4 as Curves A, B, and C respectively. Curves A and B display a monomodal molecular weight distribution. Curve C exhibits a shoulder which suggests a bimodal molecular weight distribution. This bimodal molecular weight distribution should be due to the difference between the polymerizabilities of the non-fluorinated monomer 4 and the fluorinated monomers 1a and 1b. However, this difference is not large enough as to produce a copolymer exhibiting a clear bimodal molecular weight distribution.

The copolymerizations of 1a and 1b with 1,5-bis(1-naphthoxy)pentane (5) produced copolymers of 52.7% and 49.8% yields (soluble fraction) respectively. 200 MHz $^1$H-NMR spectrum of copolymer 7b derived from 1b and 5 is presented in Figure 9.5. This $^1$H-NMR spectrum exhibits resonances due to both 1b and 5 derived structural units. The resonance due to proton I derived from 5 (2 protons from each 5 derived unit) is about 2/3 of the resonance due to the protons E and F derived from 1b (6 protons from each 1b derived unit). According to the ratio of these integrals, the average molar ratio of 1b : 5 in the resulting copolymer 7b is 1:2. That is, the copolymer 7b is richer in monomer 5 than the starting comonomer mixture.

Both copolymers 7a and 7b have bimodal molecular weight distribution. The GPC trace of the copolymer 7b is shown as Curve A in Figure 9.6. This GPC
Figure 9.3. 200 MHz $^1$H-NMR spectrum of copolymer 6a (Sample No. 2, Table 9.2) derived from 1a and 4 (an expansion of 6-9 ppm ($\delta$), in CDCl$_3$, TMS, 25 °C).
Figure 9.4. GPC traces of fluorinated polyethersulfones: A) homopolymer 2b (Sample No. 14, Table 9.1) derived from 1b; B) copolymer 3 (Sample No. 1, Table 9.2) derived from 1a and 1b; C) copolymer 6a (Sample No. 2, Table 9.2) derived from 1a and 4.
Figure 9.5. 200 MHz $^1$H-NMR spectrum of copolymer 7b (Sample No. 5, Table 9.2) derived from 1b and 5 (an expansion of 6-9 ppm (δ), in CDCl$_3$, TMS, 25 °C).
trace indicates that the copolymer 7b contains a high molecular weight fraction and
a series of oligomers.

In order to elucidate the nature of the two GPC peaks of the copolymer 7b
(Curve A, Figure 9.6), the two fractions corresponding to the individual GPC
peaks were separated by fractionation. The chloroform solution of 7b was
precipitated into 10 times excess acetone, resulting in both acetone soluble and
insoluble copolymer fractions. The GPC trace of the acetone soluble fraction is
shown as Curve B in Figure 9.6. It indicates that this fraction contains the
oligomers of copolymer 7b. The corresponding 200 MHz 1H-NMR spectrum of
the acetone soluble fraction is presented as Spectrum A in Figure 9.7. This 1H-
NMR spectrum still displays the resonances due to both monomers 1b and 5.
However, the ratio of the integral of the resonance due to proton I to that due to
protons E and F indicates that this fraction has a $1b : 5$ molar ratio of $5 : 2$. That is,
the acetone soluble fraction is richer in 1b derived units. Due to the low molecular
weight, the chain ends of this fraction can be clearly observed in the 1H-NMR
spectrum (resonances due to D and A'). This spectrum demonstrates that the
acetone soluble fraction of copolymer 7b contains chain ends derived from
monomer 1b.

The GPC trace of the higher molecular weight acetone insoluble fraction of
copolymer 7b is shown as Curve C in Figure 9.6. The corresponding 200 MHz
1H-NMR spectrum is presented as Spectrum B in Figure 9.7. The $1b : 5$ molar
ratio of this fraction is $1 : 20$ as determined from the ratio of respective integrals.
Therefore, the higher molecular weight fraction contains both structural units
derived from 1b and 5, but the structural units derived from monomer 5 dominate
this fraction.
Figure 9.6. GPC traces of fluorinated polyether sulfone 7b and its fractions: A) copolymer 7b (Sample No. 5, Table 9.2) derived from 1b and 5; B) the acetone soluble fraction of copolymer 7b; C) the acetone insoluble fraction of copolymer 7b.
Figure 9.7. 200 MHz $^1$H-NMR spectrum of the different fractions of copolymer 7b: A) the acetone soluble fraction of 7b (GPC shown as Curve B, Figure 9.6); B) the acetone insoluble fraction of 7b (GPC shown as Curve C, Figure 9.6) (an expansion of 6-9 ppm ($\delta$), in CDCl$_3$, TMS, 25°C).
These results provide an excellent example of a pair of monomers which leads to an ideal copolymerization system, i.e. \( r_1 = k_{11}/k_{15} < 1 \) and \( r_5 = k_{55}/k_{51} > 1 \). These copolymerizations proceed on two types of growing cation-radical species as shown in Scheme 9.5. The first type of cation-radical 8 is derived from monomer 1 and has a strong electron-withdrawing perfluoroalkylsulfonyl group\(^{13,14}\) attached at the 4-position of the phenoxy substituent. The perfluoroalkylsulfonyl group inductively destabilizes the cation-radical 8. Therefore, the radical cation 8 is a strong electrophile. In contrast to 8, the cation-radical intermediate 9 derived from the 1,5-bis(1-naphthoxy)pentane (5) has a strong electron-donating alkoxy substituent attached at the 1-position of the naphthalene. This alkoxy group inductively stabilizes the radical-cation and consequently makes 9 a weaker electrophile than 8. More importantly, the cation in the cation-radical 9 can be completely delocalized on the oxygen atom of the alkoxy substituent as shown in structure 10. This oxonium ion is however incapable of reacting as an electrophile due to its low reactivity.

These combined effects determine that the cation-radical 8 is much more reactive than 9. However, the reactivity of the monomers 1 is lower than that of 5 due to the higher oxidation potential of the 1. The difference between the reactivities of these monomers determines that monomer 5 is preferentially oxidized first to form the corresponding cation-radical intermediate 9, which although is stabilized still prefers to add to monomer 5 which is more reactive. However, monomer 1 can also add to the intermediate 9 at a relatively lower rate to form a copolymer linkage. The end group derived from 1 has also a lower rate of oxidation. Therefore it retards the propagation reaction. The oxidation of 1 terminated polymer molecule and its subsequent propagation can be responsible for
Scheme 9.5. Two types of radical-cation growing species during the copolymerization of 1a or 1b with 5.
the generation of a lower molecular weight copolymer fraction. Since both the more reactive and less easily formed radical-cation 8 and the less reactive but more easily generated radical-cation 9 prefer to add to the more reactive monomer 5, the final copolymer has a higher content of monomer 5 (Figure 9.5). As the copolymerization proceeds to a high conversion, the concentration of 5 decreases, and the polymerization of 1 becomes more important thus leading to a heterogeneous copolymer composition. A quantitative evaluation of this monomer pair requires the determination of the monomer reactivity ratios.

The solubilities of the polymers 2a, 2b and poly(4) in various organic solvents were determined. The results are listed in Table 9.3. The fluorinated polymers 2a and 2b are partially soluble in acetone, while the non-fluorinated analogue poly(4) is totally insoluble. An increased solubility of the fluorinated polymers was also observed in benzene and dimethyl sulfoxide.

The glass transition temperatures (Tg) of homopolymer 2a (m = 4) and 2b (m = 8) are 206 and 165°C respectively. They are much lower than the Tg of poly(4), i.e. 281°C. The decrease in the Tg of polyether sulfones containing perfluorinated segments is caused by the increased chain mobility by the flexible perfluoroalkyl groups. The chain mobility in polymer 2a (four CF₂ groups) is less than that in the polymer 2b (eight CF₂ groups), and therefore Tg decreases from 206°C in 2a to 165°C in 2b. The copolymer 3 derived from 1a and 1b has a single Tg at 171°C, which is between the Tg values of the two homopolymers. This indicates that this copolymer is a statistical copolymer. The Tg's of copolymer 6b and 7b were also between the Tg's of the respective homopolymers. The low molecular weight and high molecular weight fractions of copolymer 7b are miscible.
Table 9.3. Solubility\(^a\) of Fluorinated Polyether Sulfones.

<table>
<thead>
<tr>
<th>Solvent</th>
<th>Polymer</th>
<th></th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>2a</td>
<td>2b</td>
</tr>
<tr>
<td>Chloroform</td>
<td>++</td>
<td>++</td>
<td>++</td>
</tr>
<tr>
<td>Methylene Chloride</td>
<td>++</td>
<td>++</td>
<td>++</td>
</tr>
<tr>
<td>Tetrahydrofuran</td>
<td>++</td>
<td>++</td>
<td>+/-</td>
</tr>
<tr>
<td>o-Dichlorobenzene</td>
<td>++</td>
<td>++</td>
<td>+</td>
</tr>
<tr>
<td>Anisole</td>
<td>++</td>
<td>++</td>
<td>++</td>
</tr>
<tr>
<td>Nitrobenzene</td>
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</tr>
<tr>
<td>Benzene</td>
<td>-</td>
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<tr>
<td>Pyridine</td>
<td>++</td>
<td>++</td>
<td>++</td>
</tr>
<tr>
<td>Dimethylacetamide</td>
<td>++</td>
<td>++</td>
<td>++</td>
</tr>
<tr>
<td>Dimethyl Sulfoxide</td>
<td>+-</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>Acetone</td>
<td>+-</td>
<td>+</td>
<td>-</td>
</tr>
<tr>
<td>Methanol</td>
<td>-</td>
<td>-</td>
<td>-</td>
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</table>

\(a\) Solubility: ++: soluble at room temperature; +: soluble on heating; +/-: partially soluble or swelling; -: insoluble.
Table 9.4. Thermal Behavior of Fluorinated and Non-fluorinated Polyether Sulfones.

<table>
<thead>
<tr>
<th>Polymer</th>
<th>Glass Transition Temperature(^a) (°C)</th>
<th>Decomposition Temperature (°C)(^b) in Air</th>
<th>in Nitrogen</th>
</tr>
</thead>
<tbody>
<tr>
<td>2a</td>
<td>206</td>
<td>360 380</td>
<td>360 380</td>
</tr>
<tr>
<td>2b</td>
<td>165</td>
<td>360 390</td>
<td>365 395</td>
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<tr>
<td>Poly(4)(^c)</td>
<td>281</td>
<td>450 520</td>
<td>480 535</td>
</tr>
</tbody>
</table>

\(^a\) Determined by DSC at a heating rate of 20°C/min in nitrogen.
\(^b\) Temperature at 1% and 10% weight loss was recorded by TG at a heating rate of 10°C/min.
\(^c\) The polymer was synthesized as previously described.\(^8\)
Thermogravimetric analysis (TGA) results are listed in Table 9.4. The fluorinated polyether sulfones 2a and 2b started losing weight at 360°C. The temperatures at which 10% weight loss were observed in air or nitrogen are 380 and 390-395°C for polymer 2a and 2b respectively.

9.4. CONCLUSIONS

Polyether sulfones containing perfluoroalkylsulfonfyl groups have been synthesized by a radical-cation polymerization of 1,4-bis[4-(1-naphthoxy)phenylsulfonfyl]perfluorobutane (1a) and 1,8-bis[4-(1-naphthoxy)phenylsulfonfyl]perfluoro-octane (1b). Copolymers of fluorinated monomers 1a and 1b with 4,4′-bis(1-naphthoxy)diphenyl sulfone (4) and 1,5-bis(1-naphthoxy)pentane (5) were also synthesized. The influence of the monomer structure on the reactivities of both monomers and the growing radical-cation species was discussed. The radical-cations derived from the monomers 1a and 1b are remarkably more reactive than the radical-cation derived from 5. However, the monomer 5 is more reactive than monomers 1a and 1b. Therefore, monomer 5 is preferentially oxidized first to form a copolymer richer in 5 in overall composition than the starting monomer mixture. At the end of the copolymerization, the copolymer has a high molecular weight fraction richer in monomer 5 and a series of oligomers richer in monomer 1a or 1b.
REFERENCES


CHAPTER 10

SYNTHESIS AND CATION-RADICAL POLYMERIZATION OF 1,3- AND 1,4-BIS[4-(1-NAPHTHOXY)BENZOYL]BENZENE, BIS[4-(1-NAPHTHOXY)PHENYL]METHANE, 1,3- AND 1,4-BIS[4-(1-NAPHTHOXY)PHENYLMETHYL]BENZENE

10.1. INTRODUCTION

Aromatic nucleophilic substitution and aromatic electrophilic acylation reactions are commonly used to synthesize poly(ether ketone)s.\textsuperscript{1-4} Developments in the synthesis of poly(ether ketone)s were recently provided by two novel synthetic approaches which use different polymerization reactions. The first new procedure was achieved by applying the Scholl reaction to the polymerization of 4,4'-bis(1-naphthoxy)benzophenone to yield poly(1,1'-binaphthyl ether phenyl ketone)s.\textsuperscript{5} A cation-radical mechanism was assumed to be responsible for the C-C coupling polymerization between the aromatic rings. The glass transition temperatures of the polyether ketones prepared by the Scholl reaction\textsuperscript{5} are higher than those synthesized either by the aromatic electrophilic acylation or by the aromatic nucleophilic substitution reactions.\textsuperscript{6-9} The second new procedure was based on the Ni\textsuperscript{0} catalyzed crosscoupling reaction of various aromatic dichlorides containing ether ketone units.\textsuperscript{10}

So far, two types of monomer structures have been polymerized by the Scholl reaction (Scheme 10.1). The first type of monomer is an $\alpha,\omega$-bis(1-naphthoxy)alkanes containing various numbers of methylene groups.\textsuperscript{11,12} The
Scheme 10.1. General structure of the monomers.
second type of monomers have basically diphenyl sulfone, \(^5\) benzophenone, \(^5\) or \(\alpha,\omega\)-bis(phenylsulfonyl)perfluoroalkane groups as the central unit of the monomers.\(^{13}\) The central units of these monomers are substituted in their 4,4'-positions with polymerizable groups which include 1-naphthoxy, \(^5\) 1-phenylthio, \(^{14}\) 1-phenoxy, \(^{14}\) and the last one being either unsubstituted or substituted with various groups such as methyl, tert-butyl, methoxy and phenyl.\(^{14}\) However, there are no investigations on the Scholl polymerization of monomers containing dibenzoyl benzene, or diphenylmethane or bis(phenylmethyl)benzene central groups.

This chapter describes the synthesis and the cation-radical polymerization of 1,3-bis[4-(1-naphthoxy)benzoyl]benzene and 1,4-bis[4-(1-naphthoxy)benzoyl]-benzene, bis[4-(1-naphthoxy)phenyl]methane, 1,3-bis[4-(1-naphthoxy)phenylmethyl]benzene, and 1,4-bis[4-(1-naphthoxy)phenylmethyl]benzene. The polymerizability of these monomers containing different functional groups will be discussed based on the cation-radical mechanism of polymerization.

### 10.2. EXPERIMENTAL

#### 10.2.1. Materials

1-Naphthol (1) (99%, Lancaster Synthesis), 4,4'-difluorobenzophenone (2) (>99%, American Tokyo Kasei), fluorobenzene (>99.5%, Fluka), terephthaloyl chloride (99+%, Aldrich), isophthaloyl chloride (98%, Aldrich), anhydrous FeCl\(_3\) (Aldrich), K\(_2\)CO\(_3\), LiAlH\(_4\) and AlCl\(_3\) (all from Fisher) were used as received. Dimethyl sulfoxide (DMSO) (Fisher) was distilled from CaO. Nitrobenzene (PhNO\(_2\)) was distilled from CaH\(_2\) under nitrogen. Diethyl ether was distilled from
LiAlH₄. Toluene was distilled from Na. Chloroform was distilled from LiAlH₄. Other solvents were used as received.

10.2.2. Synthesis of the Monomers

Scheme 10.2 describes the synthesis of the monomers.

Synthesis of 1,3-Bis(4-fluorobenzoyl)benzene (3) and 1,4-Bis(4-fluorobenzoyl)benzene (4)

1,3-Bis(4-fluorobenzoyl)benzene and 1,4-bis(4-fluorobenzoyl)benzene were synthesized by the Friedel-Crafts acylation of fluorobenzene with isophthaloyl chloride and terephthaloyl chloride, respectively, according to a literature procedure.¹⁵,¹⁶ Compound 3: purity (HPLC): 99.7%, mp. 176-179 °C (Lit.¹⁵ 177.5-178.5 °C). Compound 4: purity (HPLC): 99.9%, mp. 217-218 °C (Lit.¹⁵ 218.5-219.5 °C).

Synthesis of 4,4'-Bis(1-naphthoxy)benzophenone (5)

4,4'-Bis(1-naphthoxy)benzophenone was synthesized by the etherification of 4,4'-difluorobenzophenone with 1-naphthol as described in a previous publication.⁵ Purity (HPLC): 99.3%, mp. 105-106 °C (Lit.⁵ 108.8 °C).

Synthesis of 1,3-Bis[4-(1-naphthoxy)benzoyl]benzene (6) and 1,4-Bis[4-(1-naphthoxy)-benzoyl]benzene (7)

1,3-Bis[4-(1-naphthoxy)benzoyl]benzene (6) and 1,4-bis[4-(1-naphthoxy)-benzoyl]benzene (7) were synthesized by the etherification of 3 and respectively 4 with 1-naphthol (1). An example for the synthesis of 1,4-bis[4-(1-naphthoxy)benzoyl]benzene is given below.
Scheme 10.2. Synthesis of the monomers.
1-Naphthol (7.16 g, 49.7 mmol) was dissolved in a mixture of 65 mL dry 
DMSO and 50 mL dry toluene, and K₂CO₃ (8.18 g, 59.2 mmol) was added. The 
reaction flask was equipped with a nitrogen inlet, a thermometer, and a Dean-Stark 
trap equipped with a condenser. The reaction mixture was heated at 155 °C until no 
more water was collected in the Dean-Stark trap. Then the mixture was allowed to 
cool to room temperature, and 1,4-bis(4-fluorobenzoyl)benzene (7.21 g, 22.4 
mmol) was added. The reaction mixture was stirred at 155 °C for 17 h. The cooled 
reaction mixture was poured into 2 L cold water, and extracted with 
dichloromethane three times. The combined dichloromethane solution was washed 
with 5% aqueous NaOH solution and distilled water, dried over anhydrous MgSO₄, 
and dichloromethane was removed on a rotary evaporator yielding purple crystals. 
The resulting crystals were dissolved in chloroform and subjected to a short silica 
gel column using chloroform as eluent. The residue remaining after the removal of 
chloroform was recrystallized from a mixture of methanol and chloroform to yield 
9.53 g (75%) brown crystals. Purity (HPLC): 99.9%. mp. 197-198 °C. ¹H-
NMR (CDCl₃, TMS, δ, ppm): 7.08 (d, 4H, Ph-Η ortho to the naphthoxy group), 
7.21 (d, 2H, 2-Η of the naphthalene unit), 7.36-7.65 (m, 6H, 3-, 4-, 6-Η of the 
naphthalene unit), 7.78 (d, 2H, 7-Η of the naphthalene unit), 7.84 (s, 4H, Ph-Η of 
the terephthaloyl unit), 7.85 (d, 4H, Ph-Η meta to the naphthoxy unit), 7.94 (d, 
2H, 5-Η of the naphthalene unit), 8.06 (d, 2H, 8-Η of the naphthalene unit).

1,3-Bis[4-(1-naphthoxy)benzoyl]benzene was synthesized by the same 
procedure. The crude 1,3-bis[4-(1-naphthoxy)benzoyl]benzene was purified by a 
silica gel column with benzene as eluent, yielding a glassy compound (91%). 
Purity (HPLC): 99.9%. Tg = 47 °C. ¹H-NMR (CDCl₃, TMS, δ, ppm): 7.04 (d, 
4H, Ph-Η ortho to the naphthoxy group), 7.16 (d, 2H, 2-Η of the naphthalene
unit), 7.32-7.68 (m, 7H, 3-, 4- and 6-H of the naphthalene unit and 5-H of the isophthaloyl unit), 7.74 (d, 2H, 7-H of the naphthalene unit), 7.83 (d, 4H, Ph-H meta to the naphthoxy group), 7.90-8.07 (m, 6H, 5- and 8-H of the naphthalene unit and 4- and 6-H of the isophthaloyl group), 8.13 (s, 1H, 2-H of the isophthaloyl group).

Synthesis of Bis[4-(1-naphthoxy)phenyl]methane (8), 1,3-Bis[4-(1-naphthoxy)phenylmethyl]benzene (9) and 1,4-Bis[4-(1-naphthoxy)phenylmethyl]benzene (10)

These compounds were synthesized from their corresponding ketone precursors 5, 6 and 7 by a modified LiAlH₄-AlCl₃ reduction procedure. An example for the synthesis of 1,4-bis[4-(1-naphthoxy)phenylmethyl]benzene (10) is described below.

Dry diethyl ether (60 mL) was added dropwise to an ice-water bath cooled flask containing 10.72 g AlCl₃ under nitrogen. The resulting AlCl₃ solution was added dropwise under nitrogen to a slurry of LiAlH₄ (1.38 g, 40.2 mmol) and 60 mL dry diethyl ether cooled in an ice-water bath. To this reducing solution was added dropwise a solution of 1,4-bis[4-(1-naphthoxy)benzoyl]benzene (4.56 g, 8.0 mmol) in 60 mL dry CHCl₃ under nitrogen. The reaction mixture was stirred at room temperature for 12 h. The content was poured into 200 mL ice-water mixture under vigorous stirring. The solution was filtered through Celite®, and the resulting solution was extracted three times with portions of 100 mL of benzene. The combined benzene layers were washed with water, dried over anhydrous MgSO₄, filtered and the solvent was removed on a rotary evaporator. The resulting pink oil crystallized on standing. The crude product was purified on a 20 cm basic alumina column using benzene as eluent, resulting in a colorless oil which
crystallized on standing. The product was then recrystallized from a mixture of methanol and chloroform yielding 4.34 g (70%) of white crystals. Purity (HPLC): 98.6%, mp. 143-144 °C. 1H-NMR (CDCl₃, TMS, δ, ppm): 3.94 (s, 4H, two CH₂), 6.92 (d, 2H, 2-H of the naphthalene unit), 6.97 (d, 4H, Ph-H ortho to the naphthoxy unit), 7.14 (s, 4H, Ph-H of the 1,4-diphenylbenzene unit), 7.16 (d, 4H, Ph-H meta to the naphthoxy group), 7.32-7.62 (m, 8H, 3-, 4-, 6-, and 7-H of the naphthalene unit), 7.84-7.90 (m, 2H, 5-H of the naphthalene unit), 8.20-8.24 (m, 2H, 8-H of the naphthalene unit).

The crude bis[4-(1-naphthoxy)phenylmethyl]ketone (8) was prepared by the same method as 10 and recrystallized from a mixture of methanol and chloroform yielding white crystals (88%), mp. 94.0-95.5 °C. 1H-NMR (CDCl₃, TMS, δ, ppm): 3.96 (s, 2H, CH₂), 6.94 (d, 2H, 2-H of the naphthalene unit), 6.98 (d, 4H, Ph-H ortho to the naphthoxy group), 7.17 (d, 4H, Ph-H meta to the naphthoxy group), 7.33-7.63 (m, 8H, 3-, 4-, 6-, and 7-H of the naphthalene unit), 7.85-7.90 (m, 2H, 5-H of the naphthalene unit), 8.20-8.25 (m, 2H, 8-H of the naphthalene unit).

The crude 1,3-bis[4-(1-naphthoxy)phenylmethyl]benzene (9) was also prepared by the same method as 10 and purified by column chromatography (silica gel, using benzene as eluent), yielding a white viscous liquid (87%). Purity (HPLC): 98.4%. The 1H-NMR (CDCl₃, TMS, δ, ppm): 3.92 (s, 4H, two CH₂), 6.90 (d, 2H, 2-H of the naphthalene unit), 6.96 (d, 4H, Ph-H ortho to the naphthoxy group), 7.04 (d, 2H, 4- and 6-H of the 1,3-diphenylbenzene unit), 7.13 (d, 4H, Ph-H meta to the naphthoxy group), 7.18-7.29 (m, 2H, 2- and 4-H of the 1,3-diphenylbenzene unit), 7.33-7.59 (m, 8H, 3-, 4-, 6-, and 7-H of the naphthalene unit).
unit), 7.80-7.87 (m, 2H, 5-\text{H} of the naphthalene unit), 8.20-8.24 (m, 2H, 8-\text{H} of the naphthalene unit).

10.2.3. Polymerization Reactions

The polymerization reactions are outlined in Scheme 10.3. All polymerizations were performed under nitrogen in dry nitrobenzene, using FeCl₃ as oxidant. The detailed polymerization conditions are summarized in Tables 10.1 to 10.4. A typical polymerization example is provided below.

Bis[4-(1-naphthoxy)phenyl]methane (0.45 g, 1.0 mmol) was dissolved in 0.6 mL dry nitrobenzene placed in a 25 mL three-neck flask equipped with a nitrogen inlet-outlet, and an addition funnel. A solution of 0.33 g FeCl₃ dissolved in 1.2 mL dry nitrobenzene was added dropwise under a stream of nitrogen over 20 min period. The reaction mixture was stirred at room temperature for 4 h. The content was precipitated into 200 mL methanol acidified with 2\% HCl. The precipitate was filtered and washed with boiling methanol and dried in vacuo yielding 0.44 g (97\%) polymer. The precipitate was then dissolved in 10 mL hot CHCl₃ and then precipitated into 200 mL acetone yielding a white precipitate. $\overline{M}_n$ (GPC) = 12200 g/mol, $\overline{M}_w/\overline{M}_n = 5.76$.

In several cases the progress of the polymerization reaction was monitored by GPC as described below for the Sample No. 9 from Table 10.1.

After 0.1 h, 1.0 h and 12.0 h, a syringe fitted with a 10 inch needle was first flushed with nitrogen, and a sample of 0.1 mL of the polymerization mixture was withdrawn and subsequently precipitated into 2.0 mL methanol. The separated precipitate was washed twice with methanol. Methanol was evaporated and the
Scheme 10.3. Polymerization of 1,3-bis[4-(1-naphthoxy)benzoyl]benzene (6), and 1,4-bis[4-(1-naphthoxy)benzoyl]benzene (7), bis[4-(1-naphthoxy)phenyl]methane (8), 1,3-bis[4-(1-naphthoxy)phenylmethyl]benzene (9), and 1,4-bis[4-(1-naphthoxy)phenylmethyl]benzene (10).
resulting precipitate was dried in vacuo. The dried precipitate was subjected to GPC analysis.

10.3. RESULTS AND DISCUSSION

The synthesis of 4,4'-bis(1-naphthoxy)benzophenone (5), 1,3-bis[4-(1-naphthoxy)benzoyl]benzene (6), and 1,4-bis[4-(1-naphthoxy)benzoyl]benzene (7) are outlined in eq 1 from Scheme 10.2. These reactions consist of an aromatic nucleophilic substitution reaction of 4,4'-difluorobenzophenone (2), 1,3-bis(4-fluorobenzoyl)benzene (3), and 1,4-bis(4-fluorobenzoyl)benzene (4) respectively by 1-naphthol. These reactions were performed under nitrogen at 155°C in DMSO, using K₂CO₃ as base.

The polymerization of 4,4'-bis(1-naphthoxy)benzophenone was described in a previous publication. However, there are no previous reports on the polymerization of 1,3-bis[4-(1-naphthoxy)benzoyl]benzene (6) and 1,4-bis[4-(1-naphthoxy)benzoyl]benzene (7). The polymerization of monomers 6 and 7 containing two carbonyl groups is shown in eq 3 from Scheme 10.3. This aromatic C-C coupling polymerization leads to PEEKK. These PEEKK polymers contain a bulky 1,1'-binaphthyl-4,4'-ether unit which increases the solubility and decreases the crystallinity of the resulting polymers.

The polymerization of 1,3-bis[4-(1-naphthoxy)benzoyl]benzene (6) is shown in eq 3 from scheme 10.3. These polymerizations were performed under nitrogen in dry nitrobenzene at room temperature, using FeCl₃ as oxidant. The results of these polymerizations are summarized in Table 10.1. The polymers synthesized at a FeCl₃/monomer (mol/mol) ratio of 4/1 (Exp. No. 1 and 2, Table 10.1) have number average molecular weights (Mₙ) of 2500 and 3300 g/mol, and
Table 10.1. Polymerization of 1,3-Bis[4-(1-naphthoxy)benzoyl]benzene (6) and 1,4-Bis[4-(1-naphthoxy)benzoyl]benzene (7). Polymerization Temperature, 25 °C.

<table>
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<tr>
<th>Exp. No.</th>
<th>Monomer/ (mmol)</th>
<th>PhNO₂ (mL)</th>
<th>FeCl₃ (mmol)</th>
<th>PhNO₂ (mL)</th>
<th>Reaction Time (h)</th>
<th>Polymer Yield (%)</th>
<th>$\overline{M}_n$ (g/mol)</th>
<th>$\overline{M}_w/\overline{M}_n$</th>
<th>$T_g$ (°C)</th>
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<td>45</td>
<td>3300</td>
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<td>5400</td>
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<td>51</td>
<td>3000</td>
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polydispersities ($\overline{M}_w/\overline{M}_n$) of 2.81 and 2.33, respectively. Their glass transition
temperatures are 171 and 190 °C. Another polymerization was performed at a
FeCl₃/monomer (mol/mol) ratio of 8/1 (Exp. No. 5, Table 10.1). The increase of
the FeCl₃/monomer molar ratio from 4/1 (Exp. No. 1 and 2, Table 10.1) to 8/1
(Exp. No. 5, Table 10.1) did not substantially increase the $\overline{M}_n$, but the
polydispersity has increased dramatically due to the heterogeneity of the
polymerization mixture at high FeCl₃ concentrations. Two additional
polymerization experiments were conducted at a FeCl₃/monomer molar ratio of 6/1
(Exp. No. 3 and 4, Table 10.1).

Experiment 3 (Table 10.1) was performed at a lower monomer
concentration (0.125 mol/L) and at a lower FeCl₃ concentration (1.2 mol/L). This
polymerization led to a 76% yield of polymer with $\overline{M}_n = 4700$ g/mol, $\overline{M}_w/\overline{M}_n = 1.75$. The GPC trace of the resulting polymer is shown as Curve A in Figure 10.1.
The low polydispersity of this polymer demonstrates that under appropriate
experimental conditions the Scholl reaction leads to a homogeneous polymerization.

Exp. No. 4 (Table 10.1) was performed at a higher monomer concentration (0.25
ml/L) than in Exp. No. 3. The resulting polymer was obtained with a yield of 81%,
a slightly increased $\overline{M}_n$ (5400 g/mol) and a broader molecular weight distribution
than that of the polymer obtained from Exp. No. 3. The GPC trace of the resulting
polymer is shown as Curve B in Figure 10.1. In contrast to the sharp and narrow
molecular weight distribution peak of Curve A, Curve B displays a much broader
main peak and in addition, a small peak of higher molecular weight. This
experiment demonstrates the effect of the increased monomer concentration on the
molecular weight and on the molecular weight distribution of the resulting
polymers. At low concentration of monomer and at appropriate FeCl₃/monomer
Figure 10.1. GPC traces of representative polymer 12: A) Polymer 12 prepared at FeCl₃/monomer = 6/1 (mol/mol) (Sample No. 4, Table 10.1), B) Polymer 12 prepared at a higher monomer concentration than A) (Sample No. 5, Table 10.1).
molar ratio, the polymerization medium is homogeneous and of low viscosity. This results in polymers of narrow polydispersity.

An increase in the concentration of monomer results in a heterogeneous reaction mixture. This heterogeneity causes localized domains in the polymerization medium of either higher or lower concentrations of monomers than the average monomer concentration. This effect is responsible for both the broadening of the molecular weight distribution and the appearance of high molecular weight fraction. An important conclusion derived from these experiments is that under appropriate experimental conditions the polymerization by the Scholl reaction can be performed cleanly to produce polymers of narrow polydispersity. These experiments have also demonstrated that the polymerization by the Scholl reaction should be started from a dilute monomer concentration, and the molecular weight can be optimized by increasing the concentration until the limit of the polymerization is reached as shown by the broadening of the molecular weight distribution. All the other polymerization experiments performed at higher monomer concentrations suffer from the effect of the broadening of the polymer molecular weight distribution which is caused by the heterogeneity of the reaction mixture.

Poly{1,3-bis[4-(1-naphthoxy)benzoyl]benzene} (i.e. polymer 12) is soluble in common organic solvents such as chloroform and tetrahydrofuran (THF). The structure of polymer 12 was determined by solution $^1$H-NMR spectroscopy. A typical 200 MHz $^1$H-NMR spectrum of polymer 12 (Sample No. 1, Table 10.1) is shown in Figure 10.2, along with the peak assignments. $^5,20-22$

The polymerization of 1,4-bis[4-(1-naphthoxy)benzoyl]benzene (7) is shown in eq 3 from scheme 10.3. The results of the polymerization reactions are summarized as Exp. No. 6-10 from Table 10.1. Similar observations to those
Figure 10.2. 200 MHz $^1$H-NMR spectrum (CDCl$_3$, TMS) of poly{1,3-bis[4-(1-naphthoxy)benzoyl]benzene} (12) (Sample No. 1, Table 10.1).
resulted from the polymerization of the 1,3-isomer (6) can be made here. First, the polymerization at FeCl₃/monomer molar ratios of 4/1 and 8/1 and at high monomer concentrations produced polymers of low molecular weights (2500 to 3300 g/mol) and broad molecular weight distributions ($\bar{M}_w/\bar{M}_n = 3.19$ to 4.90). Secondly, the polymerization experiments performed at a FeCl₃/monomer molar ratio of 6/1 and at lower concentrations of both monomer and FeCl₃ (Exp. No. 8 and 9, Table 10.1) led to polymers of higher molecular weights (4800 and 5400 g/mol) and narrow polydispersities (2.31 and 2.91). Thirdly, even at a FeCl₃/monomer molar ratio of 6/1, the molecular weight and polydispersity increased as the concentrations of both the monomer and FeCl₃ increased (Exp. No. 8 versus Exp. No. 9).

One of the polymerization experiments (Exp. No. 9, Table 10.1) was followed at various reaction times. The GPC traces of these samples are presented in Figure 10.3. Curve A represents the methanol insoluble fraction of the sample taken after 0.1 h of polymerization. This curve demonstrates that a high molecular weight polymer was already produced at this short polymerization time. Curves B and C show the GPC traces of the methanol insoluble fractions of the polymerization mixture after 1.0 h and 12.0 h, respectively. It is obvious that the amount of oligomers decreases with the polymerization time. A gradual shift of the polymer peak towards a higher molecular weight was noticed as the polymerization time increases (from Curve A to C). Curve D displays the GPC trace of the acetone insoluble polymer separated at the end of the polymerization (15.0 h). The acetone insoluble fraction does not contain any of the oligomers. The polydispersity of the resulting polymer is 2.91. All samples of the polymer 13 are soluble in common organic solvents. The 200 MHz $^1$H-NMR spectrum of a typical polymer 13 is shown in Figure 10.4 along with the protonic assignments.
Figure 10.3. GPC traces of samples taken at different polymerization times during the synthesis of polymer 13 (Exp. No. 9, Table 10.1): A) $t = 0.1$ h (methanol insoluble), B) $t = 1.0$ h (methanol insoluble), C) $t = 12.0$ h (methanol insoluble), D) $t = 15.0$ h (acetone insoluble) fraction.
Figure 10.4. 200 MHz $^1$H-NMR spectrum (CDCl$_3$, TMS) of poly[1,4-bis[4-(1-naphthoxy)benzoyl]benzene] (13) (Sample No. 4, Table 10.1).
A comparison of the polymerization of 1,3- and 1,4-bis[4-(1-naphthoxy)benzoyl]benzene (6 and 7) (under similar polymerization conditions, Table 10.1) exhibits comparable polymerizabilities. Higher molecular weight polymers can be synthesized by optimizing the concentrations of both the monomer and FeCl₃, and also by changing the polymerization temperature. Since the objective of these polymerizations is to investigate the polymerizabilities of the monomers 5, 6 and 7 which contain one or two carbonyl groups, no efforts have been made to maximize the average molecular weights of these polymers.

The second series of experiments were performed to investigate the polymerizability of the derivatives of 4,4'-di(1-naphthoxy)benzophenone (5), 1,3-bis[4-(1-naphthoxy)benzoyl]benzene (6) and 1,4-bis[4-(1-naphthoxy)benzoyl]benzene (7), in which the respective carbonyl group(s) were reduced to methylene (CH₂) groups. As shown in eq 2 from Scheme 10.2, the first series of monomers which contain either one carbonyl group (5) or two carbonyl groups (6 and 7) were reduced with the LiAlH₄-AlCl₃ complex.¹⁷-¹⁹ The resulting monomers 8, 9 and 10 containing either one or two CH₂ groups were polymerized by using similar reaction conditions as those in the polymerization of 5, 6 and 7 (eq 3, Scheme 10.2).

The results of the polymerization of bis[4-(1-naphthoxy)phenyl]methane (8) are listed in Table 10.2. A stoichiometric molar ratio of FeCl₃ to monomer, i.e. FeCl₃/monomer = 2/1 (mol/mol) was sufficient to produce polymer 14 with $\overline{M}_n$ in the range of 12000 to 15400 g/mol (Exp. 5-7, Table 10.2). The polymerization performed at low concentrations of both monomer and FeCl₃ (Exp. No. 1, Table 10.2) led to polymer 14 (Scheme 10.2) with narrow molecular weight distribution but relatively low $\overline{M}_n$ values (i.e. $\overline{M}_n = 4300$ g/mol). The polymerization
Table 10.2. Polymerization of Bis[4-(1-naphthoxy)phenyl]methane (8). Polymerization Temperature, 25 °C.

<table>
<thead>
<tr>
<th>Exp. No.</th>
<th>Monomer (mmol)</th>
<th>PhNO₂ (mL)</th>
<th>FeCl₃ (mmol)</th>
<th>PhNO₂ (mL)</th>
<th>Reaction Time (h)</th>
<th>Polymer Yield (%)</th>
<th>$\overline{M}_n$ (g/mol)</th>
<th>$\overline{M}_w/\overline{M}_n$</th>
<th>Tg (°C)</th>
</tr>
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<td>15400</td>
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</table>

a) The polymers contain some oligomers and these oligomers were included in the $\overline{M}_w/\overline{M}_n$ determinations.

b) Nitrobenzene (1 mL) was added at the end of the FeCl₃ solution addition, another 1 mL of nitrobenzene was added at 2 h of the polymerization.
experiments performed at high monomer and FeCl₃ concentrations (Exp. No. 7, Table 10.2) requires addition of more nitrobenzene both after all solution of FeCl₃ was added and after 2 h of polymerization. The glass transition temperatures of polymer 14 were in the range of 209 - 215 °C (Exp. No. 2-4, Table 10.2).

The molecular weight distributions of polymer 14 containing a CH₂ group in the repeating unit are generally broader than those derived from the diketone monomers 6 and 7 (Table 10.2). This effect is caused by the higher viscosity of these polymerization mixtures as observed during the polymerization experiments. The increased viscosity makes the stirring less efficient and therefore a homogeneous polymerization medium is difficult to achieve. The GPC trace of a polymer 14 (Sample No. 1, Table 10.2) is presented as Curve A in Figure 10.5. A small percentage of high molecular weight fraction is observed. This high molecular weight fraction resulted from the localized concentration effect (i.e. heterogeneity) and contributes substantially to the broadening of the molecular weight distribution.

The 200 MHz ¹H-NMR spectrum of a typical polymer 14 derived from bis[4-(1-naphthoxy)phenyl]methane (8) is shown in Figure 10.6. The ¹H-NMR spectrum corresponds to the structure 14 from Scheme 10.2. No side reactions derived from the two phenyl rings of the diphenylmethylene central unit were observed. It was previously conceived that an electron-withdrawing group such as sulfonyl or carbonyl is required in order to avoid the oxidation of these phenyl rings.⁵ This series of experiments on the polymerization of monomer 8 containing an electron-donating CH₂ group has demonstrated that the presence of an electron-withdrawing group is not a necessary requirement for the monomer in order to synthesize polymers free of side reactions resulted from the oxidation of the phenyl
Figure 10.5  Representative GPC traces of polymers containing CH₂ group(s): A) Polymer 14 (Sample No. 1, Table 10.3), B) Polymer 16 (Sample No. 4, Table 10.4).
Figure 10.6. 200 MHz 1H-NMR spectrum (CDCl₃, TMS) of poly(bis[4-(1-naphthoxy)phenyl)methane] (14) (Sample No. 3, Table 10.2).
rings. Therefore, a more expanded spectrum of monomers can be polymerized by this reaction.

The polymerization of 1,3-bis[4-(1-naphthoxy)phenylmethyl]benzene (9) is shown in eq 3 from Scheme 10.3. The results of the polymerization experiments are listed in Table 10.3. The polymerization experiments were performed at the stoichiometric molar ratios of FeCl$_3$ to the monomer, i.e. FeCl$_3$/monomer = 2/1 (mol/mol). At moderate concentrations of the monomer and FeCl$_3$, polymers 15 with $\langle$M$\rangle_n$ of 9800 and 10100 g/mol were obtained (Exp. No. 3 and 4, Table 10.3). In contrast, the $\langle$M$\rangle_n$ of the polymer 12 resulting from the unreduced diketone monomer 6 was only 2500 and 3300 g/mol for the experiments performed under the same concentrations of the monomer and FeCl$_3$ (Exp. No. 1 and 2, Table 10.1). Therefore, the transformation of the two carbonyl groups in 6 into two CH$_2$ groups in monomer 9 has increased the overall polymerizability of the monomer. The polymerization of 9 (Exp. No. 1, Table 10.3) for a short reaction time and at lower monomer concentration (Exp. No. 2, Table 10.3) provides polymers of narrower poydispersities and lower M$_n$ values. When the polymerization of 9 was performed with excess FeCl$_3$ oxidant (Exp. No. 5, Table 10.3), an insoluble polymer was obtained. Figure 10.7 displays the 200 MHz $^1$H-NMR spectrum of a typical polymer 15 (Sample No. 3, Table 10.3) along with the proton assignments.

The polymerization of 1,4-bis[4-(1-naphthoxy)phenylmethyl]benzene (10) is shown in eq 3 from Scheme 10.3. The polymerization results are summarized in Table 10.4. The molecular weights of the resulting polymers 16 are also higher than those of the polymers synthesized from the corresponding diketone monomer 7 performed under similar experimental conditions (cf. Exp. 2 and 3 in Table 10.4 with Exp. No. 6 and 7 in Table 10.4). The polymerization of a FeCl$_3$/monomer
Table 10.3. Polymerization of 1,3-Bis[4-(1-naphthoxy)phenylmethyl]benzene (9). Polymerization Temperature, 25 °C.

<table>
<thead>
<tr>
<th>Exp. No.</th>
<th>Monomer Solution</th>
<th>FeCl₃ Solution</th>
<th>Reaction Time (h)</th>
<th>Polymer Yield (%)</th>
<th>M_n (g/mol)</th>
<th>M_w/M_n</th>
<th>Tg (°C)</th>
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<tr>
<td></td>
<td>Monomer (mmol)</td>
<td>PhNO₂ (mL)</td>
<td>FeCl₃ (mmol)</td>
<td>PhNO₂ (mL)</td>
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<td>2.5</td>
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<td>97ᵇ</td>
<td>-</td>
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</table>

ᵃ) The polymer contains oligomers, these oligomers were included in the M_w/M_n determination.
ᵇ) Insoluble polymer gel was obtained.
Figure 10.7. 200 MHz $^1$H-NMR spectrum (CDCl$_3$, TMS) of poly[1,3-bis[4-(1-naphthoxy)phenylmethyl]benzene] (15) (Sample No. 3, Table 10.3).
Table 10.4. Polymerization of 1,4-Bis[4-(1-naphthoxy)phenylmethyl]benzene (10).

<table>
<thead>
<tr>
<th>Exp. No.</th>
<th>Monomer (mmol)</th>
<th>PhNO₂ (mL)</th>
<th>FeCl₃ (mmol)</th>
<th>PhNO₂ (mL)</th>
<th>Reaction Temperature (°C)</th>
<th>Reaction Time (h)</th>
<th>Polymer Yield (%)</th>
<th>$\overline{M}_n$ (g/mol)</th>
<th>$\overline{M}_w/\overline{M}_n$</th>
<th>Tg (°C)</th>
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<td>35</td>
<td>4.0</td>
<td>96b</td>
<td>-</td>
<td>-</td>
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</table>

a) The GPC trace of this polymer is presented in Curve B from Figure 10.5. The polymer contains both the high molecular weight fraction and some oligomers; the overall $M_w/M_n$ is 17.48.

b) Insoluble polymer gel was obtained.
molar ratio of 4/1 also resulted in an insoluble polymer. The GPC trace of a typical polymer 16 prepared under experimental conditions described as Exp. No. 3 from Table 10.4 is shown as Curve B in Figure 10.5. Besides the main polymer, this sample contains a substantial amount of higher molecular weight and oligomer fractions. The high molecular weight fraction results from the heterogeneity of the polymerization in a heterogeneous medium. The overall polydispersity of this polymer is 17.48. This GPC trace demonstrates the effect of the heterogeneous polymerization conditions on the molecular weight distribution of the resulting polymer. The 200 MHz $^1$H-NMR spectrum and the corresponding peak assignments of a typical sample of polymer 16 (Sample No. 3, Table 9.4) are presented in Figure 10.8.

All the polymers prepared from the monomers 8, 9 and 10 are white. In contrast, the polymers resulting from monomers containing either sulfone groups,$^{5,12-14}$ carbonyl groups,$^5$ and from monomers 6 and 7 containing two carbonyl groups are light yellow. This color is most probably due to the residual amount of FeCl$_3$ in the polymer which remains even after methanol precipitation and washing. FeCl$_3$ may form a complex with either the sulfonyl or the carbonyl groups of these monomers. This complex may also be responsible for the required FeCl$_3$/monomer molar ratio of 4/1 (mol/mol) when the monomer contains ketone (5,$^5$ 6 and 7) or sulfone groups$^{5,12-14}$ rather than the stoichiometric 2/1 ratio when the monomers do not contain these groups (i.e. 8, 9 and 10).

The above experiments have demonstrated that the replacement of two electron-withdrawing carbonyl groups from the monomers 6 and 7 with electron-donating CH$_2$ groups increases the overall polymerizability of the monomers 9 and 10. The overall polymerizability of a monomer in a cation-radical polymerization
Figure 10.8. 200 MHz 1H-NMR spectrum (CDCl₃, TMS) of poly[1,4-bis(4-(1-naphthoxy)phenyl)methyl]benzene (16) (Sample No. 3, Table 10.3).
reaction is actually determined by two opposing factors: 1) the nucleophilicity of the monomer and, 2) the reactivity of the radical-cation growing species. The radical-cation mechanism \textsuperscript{5,8,11-14} is outlined in Scheme 10.4. The first step (eq 4, Scheme 10.4) consists of the oxidation of the monomer to its cation-radical by the FeCl\textsubscript{3} oxidant. In this step, the monomers with electron-donating groups (i.e. 9 and 10) are more easily oxidized than those with electron-withdrawing groups (i.e. 6 and 7). This is determined by the lower oxidation potentials of monomers 9 and 10. However, in the second step of the polymerization (eq 5), the rate constant of the reaction is determined by both the reactivity of the cation-radical intermediates 17 and 18 and by the nucleophilicity of the monomers. A higher nucleophilicity of the monomer favors a higher rate constant in eq 5. If the cation-radical 18 behaves as an electrophile, it is less reactive than the cation-radical 17 due to its stabilization by the electron-donating CH\textsubscript{2} group. Therefore, the influence of CH\textsubscript{2} group versus carbonyl group on the rate constant of eq 5 is determined by the combined effect of these two opposing factors. The overall polymerizability of the monomer is therefore also a combined effect of both factors since the nucleophilicity of the monomer affects eqs 4 and 5 in the same direction. From the experimental results obtained with monomers 6, 7, 9 and 10, it seems that the nucleophilicity predominates these two factors. For example, the polymerizabilities of 4,4'-bis(1-naphthoxy)diphenyl sulfone versus that of 4,4'-bis(1-phenylthio)diphenyl sulfone are also controlled by the difference of nucleophilicity.\textsuperscript{14}

In the present case we can assume that the difference between the nucleophilicities of the monomers containing carbonyl versus CH\textsubscript{2} groups is higher than the difference between the reactivities of the two cation-radical growing species containing carbonyl versus CH\textsubscript{2} groups. However, for a pair of monomers with a
Scheme 10.4. The cation-radical mechanism of polymerization.
larger difference between the reactivities of the cation-radical growing species as a result of a strong stabilization on one of the growing species, the reactivity of the cation-radical controls the overall polymerizability as in the case of 4,4'-bis(1-naphthoxy)diphenyl sulfone versus 1,5-bis(1-naphthoxy)pentane.\textsuperscript{12}

The single electron transfer between the dimeric cation-radical 19 (eq 6) and the monomeric cation-radical leads to the dimeric dication 20. Alternatively, the dimeric cation-radical 19 is oxidized to its dication 20 by FeCl\textsubscript{3} oxidant. The dication 20 subsequently eliminates two protons generating a neutral C-C linkage between two aromatic rings. The repeated sequence of reactions (eq 4-8, Scheme 10.4) produces polymers.

Monomers 6 and 7 which contain two carbonyl groups have a lower nucleophilicity than monomer 5 which contains one carbonyl group. This is due to the fact that monomers 6 and 7 contain one electron-withdrawing carbonyl group per 1-naphthoxy group, while 5 has only 1/2 carbonyl group per 1-naphthoxy group. Previous polymerization results\textsuperscript{5} have shown that polymers with $M_n$ of 5000 to 38000 g/mol ($M_w/M_n = 3.2$ to 4.6) have been obtained from the polymerization of 5. The $M_n$ value increases with the increase in the concentrations of both the monomer and FeCl\textsubscript{3} oxidant. Due to the different polymerization conditions, a quantitative comparison between the monomers with one and two carbonyl groups can not be made at the present time. Based on the nucleophilicity difference a consideration of the polymerization mechanism would predict that 5 would have a higher polymerizability than the corresponding monomers 6 and 7.
10.4. CONCLUSIONS

In the previous report from this series an electron-withdrawing group (i.e. SO$_2$, CO, etc.) was inserted between the two phenyl rings of the 4,4'-bis(1-naphthoxy) substituted monomers. The role of these groups was to decrease the nucleophilicity of the internal aromatic units of these monomers and thus avoid possible side reactions resulted from the oxidation of these phenyl rings. The experimental results from this paper demonstrated that monomers containing either one or two electron-donating groups on these phenyl rings did not lead to side reactions which result from the oxidation of these internal phenyl rings. Therefore, this cation-radical reaction can be applied to the polymerization of monomers containing only aromatic ether units and opens a new synthetic avenue for the preparation of fully aromatic polyethers.

The replacement of electron-withdrawing CO groups with electron-donating CH$_2$ groups in the structure of 1,3-bis[4-(1-naphthoxy)benzoyl]benzene and 1,4-bis[4-(1-naphthoxy)benzoyl]benzene, increases the overall polymerizability of the respective monomer. This enhancement is attributed to the increased nucleophilicity of the monomers containing CH$_2$ versus CO groups. The overall polymerizability of monomers in these cation-radical polymerizations is determined by the combined effect of two opposing factors, i.e. the nucleophilicity of the monomer and the reactivity of the growing cation-radical species. The electron-donating/withdrawing nature of a substituent present in the structure of the monomer affects these two factors in opposite directions. The predominating factor is the one which leads to the largest difference between the reactivities of monomers or of their corresponding cation-radical species. These experimental results suggest that for the case of
monomers containing carbonyl and CH₂ groups, the overall polymerizability is
determined by the difference in the nucleophilicity of the monomers.

The monomers without SO₂ or CO group(s) can be polymerized by using a
stoichiometric FeCl₃/monomer molar ratio (i.e. 2/1, mol/mol). It is therefore
suggested that the excess FeCl₃/monomer molar ratio of 4/1 which is required for
the polymerization of monomers containing SO₂, CO and other electron-
withdrawing group(s) is probably caused by the formation of a complex between
FeCl₃ and the SO₂ or CO group. This complex determines through a dynamic
equilibrium the concentration of free FeCl₃ available as oxidant in the reaction
mixture.

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   783(1988).
   2189(1983).
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CHAPTER 11

AROMATIC POLYETHERS BY CATION-RADICAL POLYMERIZATION OF BIS(1-NAPHTHOXY)ARYLS AND 2,2-BIS[4-(1-NAPHTHOXY)PHENYL]PROPANE

11.1. INTRODUCTION

Aromatic polyethers contain most frequently ketones, sulfones, imides and other electron-withdrawing groups since they are required to activate the leaving groups used in aromatic nucleophilic substitution polymerization reactions,\(^1\)\(^-\)\(^9\) or are generated during aromatic sulfonylation and aroylation polymerization reactions.\(^3\)\(^-\)\(^7\)

The most notable exception from this class of polyethers is provided by poly(2,6-disubstituted-1,4-phenylene oxide)s which are synthesized either by the oxidative polymerization of 2,6-disubstituted phenols\(^9\) or by the single electron transfer catalyzed polymerization of 4-bromo-2,6-disubstituted phenol.\(^10\) The only other synthetic method which seems to be applicable to the synthesis of fully aromatic polyethers is the Ullmann reaction.\(^11\)

Recently, two novel synthetic procedures were applied to the synthesis of aromatic poly(etherketone)s and poly(ethersulfone)s. Both polymerization reactions involve the formation of a carbon-carbon bond during the polymerization process. One of them refers to the Ni(0) catalyzed homocoupling of various aromatic dihalides containing sulfone\(^12\) or ketone\(^13\) groups. The other refers to the cation-radical polymerization of various bis(aryloxy) derivatives (Scholl reaction) which was used to synthesize both poly(ethersulfone)s and poly(etherketone)s.\(^14\)
The first part of this paper is to demonstrate the development of a novel synthetic method for the preparation of fully aromatic polyethers based on the cation-radical polymerization of bis(aryloxy)aryl derivatives. The particular examples used to demonstrate this polymerization reaction refer to the synthesis and polymerization of 4,4'-bis(1-naphthroxy)biphenyl (12), 2,2'-bis(1-naphthroxy)biphenyl (13), 3,3'-bis(1-naphthroxy)biphenyl (19), and 1,3-bis(1-naphthroxy)benzene (24). The second part of this chapter is to present the cation-radical polymerization of 2,2-bis[4-(1-naphthroxy)phenyl]propane (44). Monomer 44 polymerizes by two different propagation steps, i.e. the cation-radical polymerization of naphthyl groups and transalkylation propagation initiated by H⁺FeCl₄⁻ generated from the first propagation.

11.2. EXPERIMENTAL

11.2.1. Materials

1-Bromonaphthalene (98%), 1-chloro-4-nitrobenzene (99%), 2,4-dichloronitrobenzene (97%), 2,2'-dipyridyl (99+%), ferric chloride (anhydrous, >98%), iron powder (99.9+%), nickel chloride (99%), resorcinol (99%), tetraethylammonium iodide (98%), triphenyl phosphine (99%) (all from Aldrich), anhydrous potassium carbonate, cuprous chloride (96.1%), sodium methoxide (all from Fisher), hypophosphorous acid (50% solution in water, Fluka), and 1-naphthol (99%, Lancaster Synthesis) were used as received. 2,2'-Bis(4-hydroxyphenyl)propane (97%, 4,4'-isopropylidenedipheno, bisphenol A) was recrystallized twice from toluene. Benzene, N,N-dimethylformamide (DMF), dimethyl sulfoxide (DMSO), N-methyl-2-pyrrolidinone (NMP), nitrobenzene, and toluene were distilled from CaH₂. Benzonitrile was distilled from P₂O₅. Pyridine
was distilled from NaOH pellets. Tetrahydrofuran (THF) was distilled from LiAlH₄. Ni(PPh₃)₂Cl₂ was prepared according to a literature procedure.¹⁵

11.2.2. Synthesis of Monomers

The synthesis of monomers is outlined in Schemes 11.1-11.4.

1-(4-Nitrophenoxy)naphthalene (4)

1-Naphthol (6.98 g, 48.4 mmol), anhydrous K₂CO₃ (8.05 g, 58.3 mmol), dry DMSO (100 mL) and dry toluene (100 mL) were placed into a 500 mL three-neck round bottom flask equipped with nitrogen inlet, Dean-Stark trap and condenser and the reaction mixture was heated at 160 °C. After the theoretical amount of water was collected, toluene was distilled off. The reaction mixture was allowed to cool to room temperature, 6.97 g (44.3 mmol) of 1-chloro-4-nitrobenzene was added and the reaction was stirred at 160 °C for 12 h. The cooled reaction mixture was poured into 1 L of water and extracted three times with dichloromethane. The dichloromethane layer was washed twice with 5% aqueous NaOH, and three times with water. The solution was dried over anhydrous MgSO₄ and the solvent was removed on a rotary evaporator. The resulting brown crystals were recrystallized from a mixture of ethanol and benzene to produce 9.07 g (77.3%) of brown crystals. Mp. 139-140 °C (lit.¹⁶ 141-142 °C, lit.¹⁷ 144-146 °C). ¹H-NMR (CDCl₃, δ, ppm): 7.05 (d, 2H, Ph- indonesia to NO₂), 7.21 (d, 1H, 2-H of the naphthalene unit), 7.42-7.73 (m, 3H, 3-H, 6-H, and 7-H of the naphthalene unit), 7.83 (d, 1H, 4-H of the naphthalene unit), 7.96 (d, 2H, 5-H and 8-H of the naphthalene unit), 8.23 (d, 2H, Ph-H ortho to NO₂).
1-(2-Nitrophenoxy)naphthalene (5)

1-(2-Nitrophenoxy)naphthalene was synthesized by the etherification of 1-chloro-2-nitrobenzene with 1-naphthol by following the same procedure used for the synthesis of 1-(4-nitrophenoxy)naphthalene. The resulting crude oily product was subjected to purification by column chromatography (silica gel, benzene/n-hexane 1/2 v/v). The yellow band was collected and the solvent was removed on a rotary evaporator to produce 1-(2-nitrophenoxy)naphthalene as an orange oil in 84.3 % yield. 5 was reported previously, however no information about its synthesis and characterization was presented.18 1H-NMR (CDCl₃, δ, ppm): 6.87 (dd, 1H, 6-H of the phenylene unit), 7.01 (d, 1H, 2-H of the naphthalene unit), 7.15 (td, 1H, 4-H of the phenylene unit), 7.33-7.63 (m, 4H, 5-H of the phenylene unit, 3-H, 6-H, and 7-H of the naphthalene unit), 7.69 (d, 1H, 4-H of the phenylene unit), 7.84-7.93(m, 1H, 5-H of the naphthalene unit), 8.00 (dd, 1H, 3-H of the phenylene unit), 8.08-8.20 (m, 1H, 8-H of the naphthalene unit).

1-(2-Nitro-5-chlorophenoxy)naphthalene (15)

1-(2-Nitro-5-chlorophenoxy)naphthalene was synthesized by the etherification of 1-nitro-2,4-dichlorobenzene with 1-naphthol following the synthesis of 1-(4-nitrophenoxy)naphthalene.

1-Naphthol (10.45 g, 72.5 mmol), anhydrous K₂CO₃ (12.05 g, 87.2 mmol) and 1-nitro-2,4-dichlorobenzene (15.31 g, 79.7 mmmol) were reacted at 160 °C for 2 h. The crude oily product was purified by column chromatography (silica gel, benzene/n-hexane 1/2, v/v). The yellow band was collected and the solvent was removed to give 14.59 g (61.1%) of 1-(2-nitro-5-chlorophenoxy)naphthalene (orange oil). 1H-NMR (CDCl₃, δ, ppm): 6.84 (br. s, 1H, Ph-H ortho to O), 7.07-
7.20 (m, 2H, Ph-\textbf{H} para to O and 2-\textbf{H} of the naphthalene unit), 7.42-7.67 (m, 3H, 3-\textbf{H}, 6-\textbf{H}, and 2-\textbf{H} of the naphthalene unit), 7.74-8.17 (m, 4H, Ph-\textbf{H} meta to O and 4-\textbf{H}, 5-\textbf{H} and 8-\textbf{H} of the naphthalene unit).

From the second fraction, 1.60 g (7.3%) of 1-(3-chloro-4-nitrophenoxy)naphthalene was obtained as yellow crystals. Mp. 133-136 °C. \textsuperscript{1}H-NMR (CDCl\textsubscript{3}, δ, ppm): 6.60 (m, 1H, Ph-\textbf{H} ortho to Cl), 7.01 (d, 1H, 2-\textbf{H} of the naphthalene unit), 7.34-7.65 (m, 4H, Ph-\textbf{H} para to Cl) and 3-\textbf{H}, 6-\textbf{H} and 7-\textbf{H} of the naphthalene unit), 7.73 (d, 1H, 4-\textbf{H} of the naphthalene unit), 7.81-8.00 (m, 1H, 5-\textbf{H} of the naphthalene unit), 8.23 (m, 2H, Ph-\textbf{H} ortho to NO\textsubscript{2} and 8-\textbf{H} of the naphthalene unit). The structure of these two fractions is in agreement with those obtained by the etherification of 1-nitro-2,4-dichlorobenzene with trifluoroethanol.\textsuperscript{19}

\textbf{1-(4-Aminophenoxy)naphthalene (6)}

In a 100 mL round bottom flask equipped with condenser, 1-(4-nitrophenoxy)naphthalene (3.87 g, 14.6 mmol) was dissolved in 15 mL of benzene and 8 mL of water and Fe powder (5.02 g, 90.0 mmol) was added. To the vigorously stirred mixture, 6 mL concentrated aqueous HCl was added slowly from the top of the condenser. The reaction mixture was heated to reflux temperature (the bath temperature was about 100 °C) and stirred for 20 h. The reaction mixture was cooled to room temperature and 40 mL of 25% NaOH aqueous solution was added. Benzene (20 mL) was added and the reaction mixture was stirred vigorously for 1 h. The mixture was filtered through Celite\textsuperscript{®} and Fe powder was washed with hot benzene. The filtrate was transferred into a separatory funnel and the benzene layer was separated, dried over anhydrous MgSO\textsubscript{4} and the solvent was removed on a
rotary evaporator. The oily red residue was slowly poured into a vigorously stirred 10% HCl aqueous solution (125 mL) to form the corresponding hydrochloride. The red solid was collected and washed with a small amount of chloroform. The hydrochloride was treated with 100 mL of 10% NaOH aqueous solution and stirred to liberate the free amine. Benzene (50 mL) was added to extract the amine and was stirred until all the hydrochloride was dissolved. The benzene layer was separated and dried over anhydrous MgSO₄. The solvent was removed on a rotavapor to yield a red viscous oil which crystallized on standing overnight. The yield was 2.41 g (70.3%). Mp. 53-55 °C. ¹H-NMR (CDCl₃, δ, ppm): 3.43 (s, 2H, NH₂), 6.65 (d, 2H, Ph-H ortho to NH₂), 6.76 (d, 1H, 2-H of the naphthalene unit), 6.91 (d, 2H, Ph-H meta to NH₂), 7.24-7.61 (m, 4H, 3-, 4-, 6- and 7-H of the naphthalene unit), 7.79-7.99 (m, 1H, 5-H of the naphthalene unit), 8.29-8.42 (m, 1H, 8-H of the naphthalene unit).

1-(2-Aminophenoxy)naphthalene (7)

1-(2-Aminophenoxy)naphthalene was synthesized by the reduction of 1-(2-nitrophenoxy)naphthalene by using the same procedure with that described for the synthesis of 1-(4-aminophenoxy)naphthalene. 1-(2-Aminophenoxy)naphthalene was obtained as a red oil in 95.7 % yield. ¹H-NMR (CDCl₃, δ, TMS): 3.82 (br peak, 2H, NH₂), 6.67-7.09 (m, 5H, Ph-H and 2-H of the naphthalene unit), 7.38 (d, 1H, 4-H of the naphthalene unit), 7.48-7.63 (m, 3H, 3-, 6-, and 7-H of the naphthalene unit), 7.83-7.92(m, 1H, 5-H of the naphthalene unit), 8.30-8.41 (m, 1H, 8-H of the naphthalene unit).
1-(2-Amino-5-chloro)naphthalene (16)

1-(2-Amino-5-chloro)naphthalene was synthesized by the reduction of 1-(2-nitro-5-chlorophenoxy)naphthalene by using the same procedure described for the synthesis of 1-(4-aminophenoxy)naphthalene. 1-(2-Amino-5-chloro)naphthalene was obtained as a deep red oil in 98.1% yield. $^1$H-NMR (CDCl$_3$, δ, ppm): 3.31 (br s, 2H, NH$_2$), 6.75-7.12 (m, 4H, Ph-H of the phenylene ring and 2-H of the naphthalene unit), 7.34-7.75 (m, 4H, 3-, 4-, 6-, and 7-H of the naphthalene unit), 7.86-8.00 (m, 1H, 5-H of the naphthalene unit), 8.21-8.39 (m, 1H, 8-H of the naphthalene unit).

1-(4-Chlorophenoxy)naphthalene (10)

In a 50 mL round bottom flask, was placed 1-(4-aminophenoxy)naphthalene (2.79 g, 11.9 mmol) and the content was heated at about 80 °C. To the melted amine, 10 mL of 20% HCl aqueous solution was added and vigorously stirred to form the hydrochloride, which was cooled in an ice/water bath. Sodium nitrite (0.821 g, 11.9 mL) was dissolved in 10 mL of water and kept in a refrigerator. The cold sodium nitrite solution was added in portions to the stirred suspension of the hydrochloride while the temperature of the reaction mixture was kept below 5 °C. As the sodium nitrite solution was added, the hydrochloride dissolved to form a red solution. The solution of the diazonium salt was added in portions to a cuprous chloride solution (CuCl, 1.344 g, 13.6 mmol in 10 mL concentrated aqueous HCl) which had been prepared and maintained in a refrigerator before use. The reaction mixture became very thick demonstrating the formation of the complex of CuCl with the diazonium salt. After the magnetic stirring became impossible, the mixture was stirred by a glass rod occasionally. The reaction mixture was allowed
to warm up to room temperature without any external heating and then heated at 60 °C for 2 h with occasional stirring. The reaction mixture gradually evolved nitrogen and became thinner. Then it was allowed to cool to room temperature and was extracted four times with diethyl ether. The extract was washed twice with 10% NaOH aqueous solution, twice with water, with 10 mL of 2N H₂SO₄, and finally again twice with water. The extract was dried over anhydrous MgSO₄ and the solvent was removed on a rotavapor. The brown oily residue was dissolved in a small amount of n-hexane and subjected to column chromatography (silica gel, n-hexane). 1-(4-Chlorophenoxy)naphthalene was obtained as a colorless oil (1.76 g, 58.3%). Bp. 130-135 °C/0.05 mmHg (lit.¹⁶ 148-149 °C/0.1 mmHg). Purity (HPLC): >99.9%. ¹H-NMR (CDCl₃, δ, ppm): 6.95 (d, 3H, Ph-H meta to Cl and 2-H of the naphthalene unit), 7.24-7.76 (m, 6H, Ph-H ortho to Cl, 3-, 4-, 6-, and 7-H of the naphthalene unit, a doublet due to Ph-H ortho to Cl was observed at 7.27), 7.83-7.95 (m, 1H, 5-H of the naphthalene unit), 8.11-8.24 (m, 1H, 8-H of the naphthalene unit).

1-(3-Chlorophenoxy)naphthalene (18)

The diazonium salt of 1-(3-aminophenoxy)naphthalene was prepared from 1-(2-amino-5-chlorophenoxy)naphthalene (10.11 g, 37.5 mmol) and sodium nitrite (2.60 g, 37.68 mmol) by using the same procedure as that described for the synthesis of 1-(4-chlorophenoxy)naphthalene. The solution of the diazonium salt was poured into 40 mL of hypophosphorous acid which was cooled in a refrigerator before use. The reaction mixture was kept in an ice/water bath with occasional stirring and allowed to warm up to room temperature overnight. Then it was extracted twice with diethyl ether and the extract was dried over anhydrous
MgSO₄. The solvent was removed on a rotary evaporator to yield a brown oil. The crude product was subjected to purification by column chromatography (silica gel, n-hexane). 1-(3-Chlorophenoxy)naphthalene was obtained as a colorless oil. Yield: 3.57 g (37.4%). Purity (HPLC): 83.9%. ¹H-NMR (CDCl₃, δ, ppm): 6.91 (d, 1H, 2-H of the naphthalene unit), 6.99-7.13 (m, 3H, Ph-H ortho and para to Cl), 7.25 (t, 1H, Ph-H meta to Cl), 7.37-7.61 (m, 3H, 3-, 6-, and 7-H of the naphthalene unit), 7.68 (d, 1H, 4-H of the naphthalene unit), 7.86-7.97 (m, 1H, 5-H of the naphthalene unit), 8.09-8.18 (m, 1H, 8-H of the naphthalene unit).

4,4′-Bis(1-naphthoxy)biphenyl (12)

A 50 mL three-neck round bottom flask equipped with a condenser containing a nitrogen inlet-outlet and a septum was charged with NiCl₂ (0.040 g, 0.31 mmol), PPh₃ (0.510 g, 1.94 mmol), Zn powder (0.534 g, 8.166 mmol) and 2,2′-dipyridyl (0.042 g, 0.272 mmol). The flask was evacuated under vacuum for 1 h and then was filled with nitrogen. The evacuation under vacuum and filling with nitrogen was repeated for three times. Dry DMF (4 mL) was added via a syringe through the septum of the condenser and the reaction mixture was heated at 65-70 °C with stirring for 15 minutes. The color changed gradually to red brown in about 5 minutes. Then a solution of 1-(4-chlorophenoxy)naphthalene (1.27 g, 4.98 mmol) in 3 mL of dry DMF was added to the resulting catalyst via a syringe. The reaction mixture was heated at 65-70 °C with stirring. In about 20 minutes, the reaction mixture became very thick demonstrating the formation of the coupling product. After 1.5 h, the reaction mixture was allowed to cool to room temperature and then was filtered under vacuum. The mixture of Zn powder and crude product was washed with a small amount of DMF and then was recrystallized from
benzene. 4,4'-Bis(1-naphthoxy)biphenyl was obtained as colorless needles. The yield was 1.47 g (66.8%). Purity (HPLC): >99.9%. Mp. 206-207 °C. 1H-NMR (CDCl₃, δ, ppm): 7.02 (d, 2H, 2-H of the naphthalene unit), 7.10 (d, 4H, Ph-H ortho to O), 7.37-7.67 (m, 12H, Ph-H meta to O and 3-, 4-, 6-, and 7-H of the naphthalene unit, a doublet at 7.52 can be assigned to Ph-H meta to O), 7.81-7.96 (m, 2H, 5-H of the naphthalene unit), 8.19-8.34 (m, 2H, 8-H of the naphthalene unit).

2,2'-Bis(1-naphthoxy)biphenyl (13)

2,2'-Bis(1-naphthoxy)biphenyl was synthesized by the coupling reaction of 1-(2-chlorophenoxy)naphthalene using a similar procedure to that described for the synthesis of 4,4'-bis(1-naphthoxy)biphenyl. The catalyst was prepared by the same procedure and the coupling reaction was continued for 20 h. The reaction mixture was allowed to cool to room temperature and filtered under vacuum to remove Zn powder. The filtrate was poured into 300 mL of water and extracted three times with benzene. The extract was washed with water and dried over anhydrous MgSO₄. The solvent was removed on a rotavapor and the residue was subjected to purification by column chromatography (silica gel, n-hexane). The first fraction yielded white crystals of 1-(phenoxy)naphthalene (43.4% yield, mp. 54-56 °C, lit.¹⁶: mp. 55 °C), which was probably produced by reductive elimination of the chlorine from 1-(2-chlorophenoxy)naphthalene. The second fraction collected contained PPh₃. 2,2'-Bis(1-naphthoxy)biphenyl was obtained as white crystals from the third fraction. After recrystallization from a mixture of n-hexane and chloroform, the yield was 52.1%. Mp. 147-148 °C. Purity (HPLC): 96.2%. 1H-NMR (CDCl₃, δ, ppm): 6.78 (d, 2H, 2-H of the naphthalene unit),
6.85 (d, 2H, 3-H of the biphenylene group), 7.07-7.67 (m, 14H, 3-, 4-, 6-, 7-H of the naphthalene unit and 4-, 5-, and 6-H of the biphenylene group), 7.81 (d, 2H, 5-H of the naphthalene unit), 8.16 (d, 2H, 8-H of the naphthalene unit).

3,3'-Bis(1-naphthoxy)biphenyl (19)

3,3'-Bis(1-naphthoxy)biphenyl was synthesized by homocoupling of 1-(3-chlorophenoxy)naphthalene by the same procedure as that described for the synthesis of 2,2'-bis(1-naphthoxy)biphenyl. The crude product was subjected to purification by column chromatography (silica gel, n-hexane). The first fraction produced 3.1% 1-phenoxy napthalene, the second fraction PPh₃, while 3,3'-bis(1-naphthoxy)biphenyl was separated as a colorless viscous solid from the third fraction. It was purified by column chromatography (silica gel, n-hexane). The yield was 59.2%. Tg, 20 °C. Purity (HPLC): 96.4%. ¹H-NMR (CDCl₃, δ, ppm): 6.99 (d, 4H, 2-H of the naphthalene unit and 4-H of the biphenylene group), 7.24-7.70 (m, 14H, 3-, 4-, 6-, and 7-H of the naphthalene unit and 2-, 5-, and 6-H of the biphenylene unit), 7.85-7.94 (m, 2H, 5-H of the naphthalene unit), 8.18-8.27 (m, 2H, 8-H of the naphthalene unit).

4,4'-Bis(4-chlorophenoxy)-1,1'-binaphthyl (20)

A 100 mL three-neck round bottom flask equipped with dropping funnel was charged with 1-(4-chlorophenoxy)naphthalene (1.28 g, 5.02 mmol). The flask was evacuated under vacuum and filled with nitrogen. Dry nitrobenzene (10 mL) was added, and a solution of FeCl₃ (0.987 g, 6.09 mmol) in 20 mL of nitrobenzene was added dropwise in the course of 30 minutes under stirring. The reaction was continued at room temperature for 2.5 h under nitrogen. The reaction mixture was
poured into 350 mL of methanol and the resulting white precipitate was collected by filtration. The white solid was washed with methanol and recrystallized from a mixture of methanol and chloroform to yield 0.933 g (73.3%) of colorless needles. Mp. 210-211 °C. Purity (HPLC): >99.9%. ¹H-NMR (CDCl₃, δ, ppm): 7.03 (d, 2H, 2-H of the naphthalene unit), 7.09 (d, 4H, Ph-H meta to Cl), 7.32-7.54 (m, 12H, Ph-H ortho to O and 3-, 6-, 7-, and 8-H of the naphthalene unit), 8.29 (br. d, 2H, 5-H of the naphthalene unit).

**1,3-Bis(1-naphthoxy)benzene (24)**

1,3-Bis(1-naphthoxy)benzene was synthesized by the Ullmann reaction of 1-bromonaphthalene with the disodium salt of resorcinol following literature reaction conditions.²²

In a 250 mL single-neck round bottom flask, sodium methoxide (5.3 g, 0.10 mol) was suspended in 100 mL of dry benzene by stirring under argon atmosphere. Resorcinol (5.5 g, 0.05 mmol) was subsequently added. Benzene and the resulting methanol were removed by distillation. Dry pyridine (100 mL) was added to the cooled disodium resorcinate powder followed by subsequent heating. When the reaction mixture reached the reflux temperature, 1-bromonaphthalene (41.7 g, 0.20 mol) and cuprous chloride (1.5 g, 0.015 mol) were added. The reaction was continued for 16 h at reflux temperature (115 °C).

The Ullmann reaction was followed by taking aliquots of 0.2 mL from the reaction mixture. The sample was added to 1.5 mL water, acidified with 5N aqueous HCl, extracted with 1.5 mL chloroform, and the chloroform layer was separated and dried with anhydrous MgSO₄. The chloroform solution was analyzed by HPLC. No unreacted resorcinol was observed after 16 h of reaction.
The resulting product represents a mixture containing 94% 1,3-bis(1-naphthoxy)benzene, 6% 3-(1-naphthoxy)phenol, and the excess of unreacted 1-bromonaphthalene.

The cooled reaction mixture was poured into 600 mL of water and was acidified with 5N aqueous HCl. The aqueous layer was extracted with 4 portions of chloroform (200 mL). The chloroform phase was separated and dried with anhydrous MgSO₄. Chloroform was removed on a rotary evaporator yielding a yellow-brown oil, which was distilled under vacuum (140 °C/~1 mmHg) to remove 1-bromonaphthalene. The resulting residue was dissolved in chloroform and washed with 3 portions of a solution of 2N aqueous NaOH. The chloroform layer was then dried with anhydrous MgSO₄, and evaporated on a rotary evaporator. The residue was recrystallized from a mixture of ethanol and chloroform to yield white crystals. The conversion was 100% based on resorcinol. The isolated yield of 1,3-bis(1-naphthoxy)benzene was 54%. Purity (HPLC): 99.8%, mp 105-106 °C. ¹H-NMR (CDCl₃, δ, ppm): 6.73 (s, 1H, 2-H of the phenylene unit), 6.79 (d, 2H, 4-H and 6-H of the phenylene unit), 7.03 (d, 2H, 2-H of the naphthalene unit), 7.25 (t, 1H, 5-H of the phenylene unit), 7.34-7.64 (m, 8H, 3-, 4-, 7-, and 6-H of the naphthalene unit), 7.86 (m, 2H, 5-H of the naphthalene unit), 8.16 (m, 2H, 8-H of the naphthalene unit).

**Dipotassium 2,2-Bis(4-Hydroxyphenyl)Propane (43)**

Potassium ethoxide was prepared by dissolving potassium (5.0 g, 0.128 mol) in 200 mL of absolute ethanol under nitrogen, to which was added a solution of 2,2-bis(4-hydroxyphenyl)propane (42, 14.6 g, 0.064 mol) in 30 mL of absolute ethanol was added to the resulting potassium ethoxide. The reaction mixture was
refluxed for 30 min, and the ethanol was distilled under nitrogen yielding compound 43 as a white powder (19.3 g, 99%).

**2,2-Bis[4-(1-Naphthoxy)Phenyl]Propane (44)**

2,2-Bis[4-(1-naphthoxy)phenyl]propane was synthesized by the Ullmann reaction of dipotassium 2,2-bis(4-hydroxyphenyl)propane (43) with 1-bromonaphthalene by modifying the reaction conditions of a literature procedure.

The dipotassium salt of 2,2-bis(4-hydroxyphenyl)propane (43, 6.7 g, 22 mmol) and 100 mL dry pyridine were heated to reflux temperature in a 250 mL single-neck round bottom flask. 1-Bromonaphthalene (23, 18.2 g, 88 mmol) and cuprous chloride (1.5 g, 15 mmol) were added, after which the reaction mixture was heated for at reflux temperature (115 °C) for 138 h.

The conversion of the reaction was followed by withdrawing aliquots of 0.2 mL each from the reaction mixture. The sample was added to 1.5 mL water, acidified with 5N aqueous HCl, and then extracted with 1.5 mL of chloroform. The chloroform layer was separated and dried over anhydrous MgSO₄, and then was analyzed by HPLC. After 13 h of reaction time, the aliquot contained 36% of 2,2-bis[4-(1-naphthoxy)phenyl]propane (44) and 64% 2-(4-hydroxyphenyl)-2-[4-(1-naphthoxy)phenyl]propane. The aliquot taken after 138 h of reaction contained 85% 2,2-bis[4-(1-naphthoxy)phenyl]propane (44) and 15% 2-(4-hydroxyphenyl)-2-[4-(1-naphthoxy)phenyl]propane.

The reaction mixture was collected and poured into 1.4 L of water and was acidified with 2.5 N aqueous HCl. The aqueous layer was extracted four times with chloroform (200 mL each time). The chloroform phase was separated, dried over anhydrous MgSO₄, and evaporated on a rotary evaporator yielding a brown
oil. The oil was distilled under vacuum (140 °C/1 mmHg) to remove the excess of unreacted 1-bromonaphthalene. The resulting residue was dissolved in chloroform and washed three times with 5N aqueous NaOH. The chloroform layer was dried over MgSO₄, and evaporated on a rotary evaporator. The residue was recrystallized from a mixture of ethanol and chloroform to yield 6.7 g (64%) 2,2-bis[4-(1-naphthoxy)phenyl]propane (44). Purity (HPLC): >99.9%, mp. 114-115 °C. ¹H-NMR (CDCl₃, δ, ppm): 1.69 (s, 6H, -C(CH₃)₂-), 6.93-6.99 (m, 4H, Ph-H ortho to the naphthoxy group); 7.24 (d, 4H, Ph-H meta to the naphthoxy group), 7.34-7.63 (m, 10H, 2-, 3-, 4-, 6-, and 7-H of the naphthoxy unit), 7.85-7.90 (m, 2H, 5-H of the naphthalene unit), 8.21-8.26 (m, 2H, 8-H of the naphthalene unit).

11.2.3. Cation-Radical Polymerizations

The polymerization reactions were performed in dry nitrobenzene under nitrogen using FeCl₃ as oxidant. The polymerization conditions are summarized in Tables 11.1 and 11.2. A typical polymerization example (experiment 22, Table 11.1) is provided below. 1,3-Bis(1-naphthoxy)benzene (24, 0.18 g, 0.5 mmol) was dissolved in 0.4 mL of dry nitrobenzene in a 25 mL round bottom flask equipped with a nitrogen inlet-outlet. To the vigorously stirred solution of monomer, a solution of FeCl₃ (0.20 g, 1.2 mmol) in 0.8 mL of dry nitrobenzene was added dropwise during 20 minutes via a dropping funnel. After 1 h of polymerization, 0.4 mmol of FeCl₃ in 0.4 mL PhNO₂ was added. The reaction mixture was stirred at room temperature for 6 h. The content was precipitated into 150 mL of methanol acidified with 2% hydrochloric acid. The precipitate was filtered, washed with methanol, and dried under vacuum. The yield was 0.15 g (82%). Two peaks were recorded on the GPC chromatogram. The main peak
(87.4% of total area) has $\bar{M}_n = 22400$ g/mol, $\bar{M}_w/\bar{M}_n = 2.3$. The minor peak (12.6% of total area) has $\bar{M}_n = 815900$ g/mol, $\bar{M}_w/\bar{M}_n = 2.3$.

In some cases, the progress of the polymerization was monitored by withdrawing an aliquot of the polymerization mixture and precipitating it into a mixture of methanol and acetone (1/1, v/v). The filtered precipitate was dried in vacuum and subsequently analyzed by GPC. Alternatively, the aliquot was poured into water to remove FeCl₃, followed by extraction with CHCl₃. The CHCl₃ layer was dried over anhydrous MgSO₄ and finally analyzed by GPC.

11.3. RESULTS AND DISCUSSION

11.3.1. Synthesis and Cation-Radical Polymerization of Bis(1-naphthoxy)aryl Monomers

The synthesis of monomers 12 and 13 is described in Scheme 11.1. Both compounds were prepared by the etherification of 2 and respectively 3 with 1 followed by the reduction of the resulting nitro derivatives 4 and 5 to the corresponding amines 6 and 7. The amines 6 and 7 were transformed into the corresponding diazonium salts 8 and 9 which were transformed into the chloride derivatives 10 and 11. Compound 4 was previously prepared in 9 to 12% yield by reacting p-nitrophenol with 1-bromonaphthalene under Ullmann reaction condition. Attempts to prepare compound 5 under similar conditions did not yield any product. However, 5 was reported previously. No analytical data and information about the synthetic procedure used in its preparation were provided.

Compounds 10 and 11 were previously synthesized under Ullmann reaction conditions by reacting 2- and 4-chlorophenol with 1-bromo-
Scheme 11.1. Synthesis of 4,4'-bis(1-naphthoxy)biphenyl (12) and 2,2'-bis(1-naphthoxy)biphenyl (13).
naphthalene.\textsuperscript{16,20} Both compounds were obtained in yields lower than 18\%. The synthetic procedures described here are more convenient and lead to products 10 and 11 in higher yields than the methods reported previously. 12 and 13 were synthesized by a Ni(0) catalyzed homocoupling of 10 and respectively 11. The Ni(0) catalyst was generated \textit{in situ} according to a literature procedure.\textsuperscript{21}

Monomer 19 was synthesized by the sequence of reactions outlined in Scheme 11.2. The essential product is 18 which can not be synthesized by the etherification of 1 with 1-chloro-3-nitrobenzene since the chloride group is not activated towards nucleophilic displacement by a nitro group present in the meta position. Therefore 18 was prepared by the sequence of reactions outlined in Scheme 11.2. This procedure is based on the etherification of 14 with 1 which was assumed to lead to a mixture of 15 and 16 containing mostly the isomer 15. This assumption was based on literature information which showed that the etherification of 14 with trifluoroethanolate led to a 75/25 mixture of the ortho versus para substituted derivatives.\textsuperscript{19} The other steps are based on conventional reactions.

Monomer 20 was synthesized by the cation-radical dimerization of 10 in nitrobenzene by using FeCl\textsubscript{3} as oxidant (Scheme 11.3).

Finally, monomer 24 was synthesized by the Ullmann reaction (Scheme 11.4) of resorcinol (21) with 1-bromonaphthalene (23) by using literature reaction conditions.\textsuperscript{22}

The cation-radical polymerization of 4,4'-bis(1-naphthoxy)biphenyl (12), 2,2'-bis(1-naphthoxy)biphenyl (13), 3,3'-bis(1-naphthoxy)biphenyl (19), and 1,3-bis(1-naphthoxy)benzene (24) is outlined in Scheme 11.5. All polymerizations were performed under nitrogen in dry nitrobenzene, using FeCl\textsubscript{3} as oxidant. The
Scheme 11.2. Synthesis of 3,3'-bis(1-naphthoxy)biphenyl (19).
Scheme 11.3. Synthesis of 4,4'-bis(4-chlorophenoxy)-1,1'-binaphthyl (20).
Scheme 11.4. Synthesis of 1,3-bis(1-naphthoxy)benzene (24).
results of these polymerizations are summarized in Table 11.1.

The polymerization experiments of 4,4'-bis(1-naphthoxy)biphenyl (12) are listed as experiments 1-5 from Table 11.1. Due to the low solubility of monomer 12 in nitrobenzene, low monomer concentration and elevated temperature were required to completely dissolve the monomer. At a FeCl₃/12 = 2/1 (mol/mol) (experiment 1, Table 11.1), the polymerization results in polymer 25 (Scheme 11.5) of $M_n = 4900$ g/mol and $M_w/M_n = 5.8$ in 58% polymer yield. The glass transition temperature (Tg) of the polymer was 235 °C. Since the monomer concentration is limited by its low solubility, attempts to increase the molecular weights of the resulting polymers by conducting polymerizations at higher FeCl₃/12 molar ratios failed (experiments 2-4, Table 11.1). These polymerizations led to an insoluble polymer. An attempt to polymerize monomer 12 in an alternative polymerization solvent (experiment 5, Table 11.1), i.e. benzonitrile, did not produce any polymer.

The solubility of polymer 25 is higher than that of its parent monomer 12. Polymer 25 is soluble in common organic solvents such as chloroform and tetrahydrofuran. The structure of polymer 25 was determined by $^1$H-NMR spectroscopy. Representative 200 MHz $^1$H-NMR spectra of monomer 12 and polymer 25 along with the peak assignments\textsuperscript{24} are presented as spectra A and B in Figure 11.1. These spectra demonstrate that the polymer obtained from 12 has the structure 25 from Scheme 11.5.

The synthesis of polymer 25 was also achieved by the Ni(0) catalyzed homocoupling reaction of 4,4'-bis(4-chlorophenoxy)-1,1'-binaphtyl (20) as outlined in Scheme 11.6. The results of these polymerization experiments are summarized in Table 11.2. Two different experimental approaches were used for
Scheme 11.5. Cation-radical polymerization of 4'-bis(1-naphthoxy)biphenyl (12), 2,2'-bis(1-naphthoxy)biphenyl (13), 3,3'-bis(1-naphthoxy)biphenyl (19), and 1,3-bis(1-naphthoxy)benzene (24).
<table>
<thead>
<tr>
<th>Exp. No.</th>
<th>Monomer/PhNO₂ (mmol/mL)</th>
<th>FeCl₃/PhNO₂ (mmol/mL)</th>
<th>Reaction Temperature (°C)</th>
<th>Reaction Time (h)</th>
<th>Polymer Yield (%)</th>
<th>N₃ (g/mol)</th>
<th>Mₘ/Mₙ</th>
<th>Tg (°C)</th>
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<td>1</td>
<td>12/1.0</td>
<td>2.0</td>
<td>115</td>
<td>5.0</td>
<td>38</td>
<td>4900</td>
<td>5.8</td>
<td>235</td>
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<td>2</td>
<td>12/0.5</td>
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<td>95</td>
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<td>.5</td>
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<td>-</td>
</tr>
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<tr>
<td>7</td>
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<td>7300</td>
<td>3.0</td>
<td>-</td>
</tr>
<tr>
<td>8</td>
<td>13/0.5</td>
<td>1.2</td>
<td>25</td>
<td>5.0</td>
<td>97</td>
<td>7300</td>
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<td>222</td>
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<td>5.3</td>
<td>235</td>
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<td>-</td>
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</tr>
<tr>
<td>13</td>
<td>19/0.5</td>
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<tr>
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<tr>
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<td>17</td>
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<td>18</td>
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<td>25</td>
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<td>20</td>
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<td>25</td>
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<td>22</td>
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<td>5.0</td>
<td>93</td>
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<tr>
<td>23</td>
<td>24/0.5</td>
<td>1.2</td>
<td>25</td>
<td>5.0</td>
<td>93</td>
<td>-</td>
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<td>-</td>
</tr>
<tr>
<td>24</td>
<td>24/0.5</td>
<td>1.2</td>
<td>25</td>
<td>5.0</td>
<td>93</td>
<td>-</td>
<td>-</td>
<td>-</td>
</tr>
</tbody>
</table>

a) Insoluble polymer was obtained.
b) Benzoinitrile was the polymerization solvent in this case.
c) Two other minor peaks were observed on the GPC chromatogram. The first peak: Mₙ = 3613000 g/mol; Mₘ/Mₙ = 1.19 (5.4% of the total area). The second peak: Mₙ = 2900 g/mol; Mₘ/Mₙ = 1.12 (15.6% of total area).
d) One additional minor peak was recorded on the GPC chromatogram: Mₙ = 3100 g/mol; Mₘ/Mₙ = 1.14 (19.6% of total area).
e) In experiments 22 and 23, 1.2 mmol and 1.7 mmol of FeCl₃ were respectively added at the beginning of the polymerizations. After 1 h of polymerization, additional 0.4 mmol and 0.3 mmol of FeCl₃ were added respectively.
f) This is the main peak on GPC. Another minor peak (12.6% of total area) with Mₙ = 815900 g/mol; Mₘ/Mₙ = 2.31 was also recorded on the GPC chromatogram.
g) Another high molecular weight fraction (5% of total area) with Mₙ = 2770800 g/mol; Mₘ/Mₙ = 2.52 was observed on the GPC chromatogram.
h) FeCl₃ (0.6 mmol) was added at the beginning of the polymerization, additional 0.2 mmol FeCl₃ was added after 6 h of polymerization.
i) A high molecular weight fraction (2% total area) with Mₙ = 3077100 g/mol; Mₘ/Mₙ = 1.20 was observed on the GPC chromatogram.
Figure 11.1. 200 MHz $^1$H-NMR spectra (CDCl$_3$, TMS) of 4,4'-bis(1-naphthoxy)biphenyl (12, Spectrum A) and poly[4,4'-bis(1-naphthoxy)biphenyl] (25, Spectrum B, Sample 1, Table 11.1). (An expansion of the $\delta = 6.5-8.5$ ppm region).
the Ni(0) catalyzed polymerization of 20. In the first method,\textsuperscript{12} a solution of the monomer 20 in NMP was added to the DMF solution of the Ni(0) catalyst generated from NiCl\textsubscript{2}, PPh\textsubscript{3}, Zn powder and 2,2'-dipyridyl. These polymerizations (experiments 1-3, Table 11.2) led to polymer 25 with a maximum yield of 60\%, and $\overline{M}_n$ in the range of 3700 to 5500 g/mol. The Tg of the polymer 25 synthesized by Ni(0) catalyzed polymerization of 20 (sample 3, Table 11.2) is 231 °C and agrees with the Tg of the polymer 25 prepared by the cation-radical polymerization of monomer 12 (experiment 1, Table 11.1).

Representative GPC traces of the polymer 25 obtained after 1 h, 5 h and 24 h of polymerization time are presented as curves A, B, and C in Figure 11.2. Even though oligomers are present in all these polymers, it is obvious that the average molecular weight shifts towards higher values as the Ni(0) catalyzed polymerization proceeds.

Due to the low solubility of monomer 20 in the reaction mixture, the polymerization (experiment 4, Table 11.2) in DMF resulted in a polymer 25 with $\overline{M}_n$ of maximum 3200 g/mol. The heterogeneity of the polymerization system has significantly broadened the polydispersity of the resulting polymer, i.e. $\overline{M}_w/\overline{M}_n = 6.4$.

The second Ni(0) polymerization procedure consists of the addition of monomer solution in THF to the Ni(0) catalyst generated from Ni(PPh\textsubscript{3})\textsubscript{2}Cl\textsubscript{2}, Et\textsubscript{4}NI and Zn powder in THF.\textsuperscript{23} However, after 24 h of polymerization, this method produced polymer 25 in only 8\% yield. The resulting polymer has a $\overline{M}_n$ of 2200 g/mol and a polydispersity of 4.0.

The synthesis of poly[4,4'-bis(1-naphthoxy)biphenyl] (25) by the cation-radical polymerization of 12 (Scheme 11.5) led to polymer 25 of a $\overline{M}_n$ lower than
Scheme 11.6. Ni(O) catalyzed coupling polymerization of 4,4'-bis(4-chlorophenoxy)-1,1'-binaphthyl (20).
Table 11.2. Polymerization of 4,4'-Bis(4-chlorophenoxy)-1,1'-binaphthyl (20).

<table>
<thead>
<tr>
<th>Exp. No.</th>
<th>Monomer (mmol)</th>
<th>Solvent/ (mL)</th>
<th>Catalyst/ (Ni mmol)</th>
<th>Solvent/ (mL)</th>
<th>Temperature (°C)</th>
<th>Reaction Time (h)</th>
<th>Reaction Yield (%)</th>
<th>Polymer (g/mol)</th>
<th>$M_n$</th>
<th>$M_w/M_n$</th>
<th>Tg (°C)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>1.0</td>
<td>DMF/1.0</td>
<td>A/0.1</td>
<td>NMP/9.0</td>
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<td>1.5</td>
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<td>-</td>
</tr>
<tr>
<td>2</td>
<td>1.0</td>
<td>DMF/1.0</td>
<td>A/0.1</td>
<td>NMP/9.0</td>
<td>75</td>
<td>5.0</td>
<td>-</td>
<td>5000</td>
<td>2.9</td>
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<td>-</td>
</tr>
<tr>
<td>3</td>
<td>1.0</td>
<td>DMF/1.0</td>
<td>A/0.1</td>
<td>NMP/9.0</td>
<td>75</td>
<td>24.0</td>
<td>60</td>
<td>3500</td>
<td>2.4</td>
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<td>-</td>
</tr>
<tr>
<td>4</td>
<td>1.0</td>
<td>DMF/1.0</td>
<td>A/0.1</td>
<td>DMF/1.0</td>
<td>75</td>
<td>4.0</td>
<td>58</td>
<td>3200</td>
<td>6.4</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>5</td>
<td>1.0</td>
<td>THF/2.0</td>
<td>B/0.1</td>
<td>THF/10</td>
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<td>24.0</td>
<td>8</td>
<td>2200</td>
<td>4.0</td>
<td>-</td>
<td>-</td>
</tr>
</tbody>
</table>

a) Catalyst A: NiCl$_2$/PPh$_3$/Zn/2,2'-dipyridyl.
Catalyst B: Ni(PPh$_3$)$_2$Cl$_2$/Et$_4$I/Zn.
Figure 11.2. GPC traces of poly[4,4'-bis(1-naphthoxy)biphenyl] (25) as a function of the polymerization time: A) t = 1 h; B) t = 5 h; C) t = 24 h.
5000 g/mol. This low \( \overline{M}_n \) was determined by the low solubility of the monomer 12. Therefore, monomers 13, 19 and 24 of higher solubilities than monomer 12 were synthesized and polymerized under similar reaction conditions.

The results of the polymerization of 2,2'-bis(1-naphthoxy)biphenyl (13) are listed as experiments 6-12 from Table 11.1. Polymerization experiments 6 to 8 from Table 11.1 were performed at low monomer concentrations and a \( \text{FeCl}_3/13 = 2.4/1 \) (mol/mol). These polymerizations produced polymers of yields ranging from 85 to 86%. The number average molecular weights of the polymers are ranging from 7000 to 7300 g/mol and their polydispersities from 2.1 to 3.1. A representative GPC trace of polymer 26 (experiment 8, Table 11.1) is shown in Figure 11.3. The polymerization performed at higher monomer concentration (experiment 9, Table 11.1) resulted in a polymer 26 with \( \overline{M}_n \) of 13900 g/mol and a polydispersity of 5.3. The glass transition temperature of this polymer is 235 °C.

2,2'-Bis(1-naphthoxy)biphenyl (13) was also polymerized at higher \( \text{FeCl}_3/13 \) molar ratios (experiments 10 and 11, Table 11.1). These polymerizations produced polymers of higher molecular weights. Their \( \overline{M}_n \) values were in the range of 85100 to 90500 g/mol. However, in addition to the main elution trace these two polymers displayed additional peaks on their GPC chromatograms. The heterogeneity of the polymerization medium at a higher monomer concentration and at higher \( \text{FeCl}_3/13 \) molar ratios are the cause of the appearance of these additional peaks. Previous polymerization experiments performed with 1,3-bis[4-(1-naphthoxy)benzoyl]benzene have demonstrated a similar effect of the monomer concentration and \( \text{FeCl}_3/\text{monomer} \) molar ratio on the molecular weight distribution of the resulting polymers.\(^{14}\) The polymerization of monomer 13 performed in benzonitrile (experiment 12, Table 11.1) failed.
\[ \bar{M}_n = 7300 \text{ g/mol} \]
\[ \bar{M}_w/\bar{M}_n = 3.1 \]

Figure 11.3. GPC trace of poly[2,2'-bis(1-naphthoxy)biphenyl] (26, Sample 8, Table 11.1).
3,3'-Bis(1-naphthoxy)biphenyl (19) was polymerized at a FeCl₃/19 molar ratio of 2.4/1 (experiments 13 and 14, Table 11.1), to yield polymer 27 with $\overline{M}_n$ of 12600 and 13300 g/mol. These experiments were performed with identical monomer and FeCl₃ concentrations as those used in the polymerization of monomer 13 (experiments 6 and 7, Table 11.1). The molecular weights of polymers derived from 19 are significantly higher than those derived from 13. The polymerization of 19 at a higher FeCl₃/19 molar ratio (experiment 16, Table 11.1) resulted in a polymer 27 of higher molecular weight, i.e. 34000 g/mol.

1,3-Bis(1-naphthoxy)benzene (24) is a monomer which has a meta-phenylene central unit instead of the biphenyl central unit. The polymerization of monomer 24 at a FeCl₃/24 molar ratio of 2.4/1.0 (experiments 17-19, Table 11.1) led to polymers with $\overline{M}_n$ up to 5400 g/mol. However, attempts to polymerize monomer 24 at FeCl₃/24 molar ratios of 3.2/1.0 and 3.8/1.0 (experiments 20 and 21, Table 11.1) produced an insoluble polymer. Subsequently, we have modified the procedure used in the addition of the FeCl₃ solution (experiments 22 to 24, Table 11.1) and obtained polymer 28 with $\overline{M}_n$ from 13800 to 22400 g/mol. This modification consists of the addition of 2.2 to 2.4 equivalents of FeCl₃ to the monomer at the beginning of the polymerization followed by subsequent addition of more FeCl₃ oxidant after respectively 1 h and 6 h of polymerization time. However, the resulting polymers displayed additional minor peaks on the molecular weight distribution presumably as a result of the heterogeneity of the polymerization medium.

The 200 MHz $^1$H-NMR spectra of 1,3-bis(1-naphthoxy)benzene (24) and of a representative poly[1,3-bis(1-naphthoxy)benzene] (28) (sample 22, Table 11.1) are presented as spectra A and B from Figure 11.4. Even though this
polymer displays a minor peak (12.6% of total area) of higher molecular weight ($\bar{M}_n = 815900$ g/mol) on its GPC trace, the polymer exhibits an expected $^1$H-NMR spectrum which agrees with the structure 28 (Scheme 11.5). The change in the shielding effect from monomer 24 to polymer 28 causes an inversion of the resonances of protons A and B. Thus in monomer 24 A is upfield from B while in polymer 28 B is upfield from A. The integral of the resonance of proton A in 28 (s, 7.00 ppm) is half of that due to the proton B (d, 6.90 ppm). This indicates the absence of any possible 5-membered ring formation between the phenylene unit and the neighboring naphthalene unit, i.e. benzonaphthofuran ring.

The polymerization of 1,3-bis(1-naphthoxy)benzene (24) was monitored by taking samples which were subsequently analyzed by GPC. Figure 11.5 shows the GPC traces of the polymers obtained at different polymerization times. Curve A represents the GPC trace of the polymer 28 after 5 min of polymerization time. The sample was obtained by precipitating the polymerization aliquot into a mixture of methanol/acetonitrile = 1/1 (v/v). This polymer has a $\bar{M}_n$ of 6300 g/mol and a polydispersity of 3.0. Therefore, this demonstrates that the polymerization of 1,3-bis(1-naphthoxy)benzene is very fast. In fact, all polymerizations performed at high monomer concentrations had to be diluted with polymerization solvent immediately after the complete dropwise addition of FeCl$_3$ solution in order to maintain an efficient stirring. As soon as a drop of FeCl$_3$ solution was added to the polymerization mixture containing monomer 24, a large amount of HCl gas evolved immediately from the polymerization mixture.

Curve B is due to a sample of polymer 28 taken after 30 minutes of reaction time. However, this sample was separated by precipitating the polymerization aliquot into water, followed by extraction with CHCl$_3$. By this method, FeCl$_3$ is
Figure 11.4. 200 MHz $^1$H-NMR spectra (CDCl$_3$, TMS) of 1,3-bis(1-naphthoxy)benzene (24, Spectrum A) and poly[1,3-bis(1-naphthoxy)benzene] (28, Spectrum B, Sample 22, Table 11.1). (An expansion of the $\delta = 6.5-8.5$ ppm region).
Figure 11.5. GPC traces of poly[1,3-bis(1-naphthoxy)benzene] (28) separated at different polymerization times of 1,3-bis(1-naphthoxy)benzene (24): A) t = 5 minutes, by precipitating the aliquot into methanol/acetone = 1/1, v/v; B) t = 30 min, by precipitating the aliquot into water and extracting with CHCl₃; C) t = 60 minutes, by precipitating the aliquot into methanol/acetone = 1/1, v/v; D) t = 390 minutes, by precipitating the aliquot into methanol/acetone.
transferred into the aqueous phase and the unreacted monomer and oligomers (both soluble in CHCl₃) are separated from the reaction mixture. Samples of polymer 28 separated by precipitation in methanol/acetone contain less monomer and oligomers. After 30 minutes of polymerization time the amount of unreacted monomer was 1.5%. Curve C represents the GPC trace of a sample separated after 60 minutes of polymerization time. This sample was separated by precipitating the sample of the reaction mixture in methanol/acetone. This polymer has a $\overline{M}_n$ of 6900 g/mol and a $\overline{M}_w/\overline{M}_n$ value of 3.8. Besides the main polymer, Curve C shows a trace of high molecular weight fraction which is responsible for the broadened polydispersity of the polymer. The polymerization was continued and additional 0.2 mmol of FeCl₃ (i.e. 0.67 equivalents of the monomer) was introduced after 300 minutes of polymerization. Curve D displays the polymer sample taken 30 minutes after the second FeCl₃ addition (i.e. after 390 minutes of polymerization time). The GPC trace of this polymer exhibits two peaks. The main peak (98% of total area) has a $\overline{M}_n$ of 14800 g/mol and a $\overline{M}_w/\overline{M}_n$ of 4.4. The minor peak (2% of total area) has a relative number average molecular weight (versus polystyrene standards) of about $3 \times 10^6$ g/mol. In fact, all the polymers prepared by the two-step addition of FeCl₃ oxidant display this type of bimodal molecular weight distribution (experiments 22-24, Table 11.1). The relative molecular weights of these high molecular weight fractions are listed in the footnotes in Table 11.1.

The analysis of the molecular weight distribution versus polymerization time dependence (Figure 11.5) has shown that the polymer separated at an early stage of the polymerization has a monomodal molecular weight distribution. Due to the high rate of polymerization, the monomer concentration decreases rapidly and the viscosity of polymerization mixture increases. This makes the monomer and FeCl₃...
oxidant concentrations not uniform throughout the polymerization system. As a result, a small fraction of high molecular weight which does not fit the main polymer peak emerges as a minor shoulder (i.e., after about 60 minutes of reaction time, Curve C, Figure 11.5). The high molecular weight fraction increases and forms a different molecular weight distribution (i.e. as a separate peak on GPC trace, Curve D, Figure 11.5) as a result of the addition of more FeCl₃ oxidant.

The structures of the other monomers containing 1-naphthoxy polymerizable groups and investigated in our laboratory¹⁴ are summarized in Scheme 11.7. The polymerization results of monomers 12, 13, 19 and 24 have demonstrated that these monomers are highly reactive in these cation-radical polymerizations. A comparison of the present results with those of the polymerizations of the other monomers suggests that the monomers containing substituted biphenyl (12,13, and 19) and phenylene (24) groups as the central units exhibit a comparable polymerizability to that of monomers 29-31 (Scheme 11.7). However, the polymerizability of the monomers 12, 13, 19, and 24 is higher than that of monomers 32-34 (Scheme 11.7).

The cation-radical dimerization of anisole, 4-methoxybiphenyl and other related compounds was investigated by electrochemical techniques.²⁵ Based on kinetic data obtained by Derivative Cyclic Voltammetry (DCV),²⁵ the two mechanisms outlined in Scheme 11.8 were proposed for their dimerization. The first mechanism is a radical-radical coupling (RRC) reaction, in which two cation-radicals dimerize to produce a dimeric dication in a single step as outlined in eq 17. The second mechanism consists of the radical-substrate coupling (RSC) leading to a dimeric cation-radical (eq 18), followed by a single electron transfer from the dimeric cation-radical to the monomeric cation-radical to generate a dimeric dication
Scheme 11.7. The structure of bis(1-naphthoxy) substituted monomers.
\[ M \xrightarrow{-e} M^+ \]  

(7)

Radical-Radical Coupling (RRC):

\[ M^+ + M^+ \xrightarrow{k_1} M \rightarrow M^{2+} \]  

(8)

Radical-Substrate Coupling (RSC):

\[ M^+ + M \xrightarrow{k_2} M \rightarrow M^+ \]

\[ M \rightarrow M^+ + M^+ \xrightarrow{k_3} M \rightarrow M^{2+} + M \]  

(10)

\[
\text{Rate} = \frac{k_2k_3[M^+]^2[M]}{k_{-2} + k_3[M^+]} 
\]

(11)

Scheme 11.8. Two mechanisms proposed for the cation-radical reactions.
and the neutral substrate (eq 19). Recent studies suggest that out of these two mechanisms only the radical-substrate coupling (RSC) (eqs 18 and 19, Scheme 11.8) is responsible for the dimerization reaction. The derived rate law for the RSC mechanism is outlined in eq 20 from Scheme 11.8. The calculated rate constants by the reaction order approach for $M = 4$-methoxybiphenyl are: $k_2 = 4.14 \times 10^4 \, M^{-1}s^{-1}$, $k_{-2} = 2.98 \times 10^6 \, s^{-1}$ and $k_3 = 10^{10} \, M^{-1}s^{-1}$ (this step was assumed to be diffusion controlled). Since $k_3 = 3 \times 10^3 \, k_{-2}$, at high substrate concentration, the overall rate of reaction reduces to $k_2[M^+]\,[M]$, i.e. the forward reaction of eq 18 is the rate determining step. At low substrate concentration, the overall rate reduces to $k_3[MM^+]\,[M^+]$, i.e., eq 19 becomes the rate determining step. The concentration at which the rate determining step changes is $2.98 \times 10^{-4} \, M$. Subsequently all the available kinetic data could be explained in terms of the RSC mechanism alone.

Based on these results, the most probable cation-radical polymerization mechanism of monomers 12, 13, 19 and 24 is presented in Scheme 11.9. The single electron transfer oxidation of monomer 35 by FeCl$_3$ leads to its corresponding cation-radical 36 (eq 21). This reaction proceeds most probably by the excitation of an EDA complex 35:FeCl$_3$. The radical-substrate coupling (eq 22) results in the dimeric cation-radical 37, which gets oxidized through the one electron transfer reduction of the monomeric cation-radical 36 to produce the dication 38. The transfer of one electron from the dimeric cation-radical 37 to the monomeric cation-radical 36 is favored since the cation-radical of 1,1'-dinaphthyl 37 is more easily oxidized than the monomeric naphthoxy cation-radical 36. This is supported by the fact that the dimer derived from anisole is more easily oxidized than anisole itself. However, in this oxidation reaction, an alternative electron transfer reaction (eq 25) is possible. It consists of one electron transfer from the
Scheme 11.9. Cation-radical mechanism for the polymerization of bis(1-naphthoxy)aryl monomers (12, 13, 19, and 24).
dimeric cation-radical 37 to the FeCl₃ oxidant. Due to the presence of an equivalent amount of FeCl₃ to monomer in the polymerization reaction and due to the probably higher electronic affinity of FeCl₃ than that of the monomeric cation-radical 36, the reaction from eq 25 might be at least as favorable as the reaction from eq 23. The dication 38 eliminates two protons to generate the neutral dimer 39 (eq 24).

A critical evaluation of the relative importance between reactions from eqs 23 and 25 requires the analysis of the kinetic data of this polymerization. The present results are not sufficient to discriminate between these two reactions.

The previous mechanisms suggested for this polymerization¹⁴ did not take into consideration the single electron transfer step from eq 23. It was proposed that the dimeric cation-radical 37 first eliminates one proton (eq 26). The resulting radical 40 is oxidized by one electron transfer to FeCl₃ to produce the dimeric monocation 41 (eq 27) which subsequently eliminates the second proton to produce the neutral dimer 39 (eq 28). The sequence of reactions from eqs 25 to 28 can be eliminated only if we demonstrate that the dication 38 (eq 23) and the cation-radicals 36 and 37 are the only active species in this reaction. Presently we do not have experimental data which can discriminate between these two polymerization mechanisms.

The initial monomer concentration in these cation-radical polymerizations ranges from 0.9 to 1.4 M. If this polymerization proceeds through the sequence of eqs 20 to 23, this concentration is significantly higher than the concentration at which the one electron transfer (eq 19 in Scheme 11.8, and eq 23 in Scheme 11.9) becomes the rate-determining step. Therefore, under these conditions, in the early stages of this polymerization, the forward reaction of eq 22 should represent the rate-determining step. As the polymerization proceeds, the decrease in the
monomer concentration may make the one electron transfer from eq 23 the rate-determining step.

The synthesis and polymerization of 4,4'-, 3,3', and 2,2'-bis(1-naphthoxy)biphenyls and of 1,3-bis(1-naphthoxy)benzene have demonstrated that the cation-radical polymerization of bis(1-naphthoxy)aryls represent a novel and general method for the synthesis of fully aromatic polyethers.

11.3.2. Cation-Radical Polymerization of 2,2-Bis[4-(1-Naphthoxy)Phenyl]Propane (44)

The synthesis of 2,2-bis[4-(1-Naphthoxy)phenyl]propane (44) is described by eqs 29 and 30 from Scheme 11.10. The reaction consists of the Ullmann crosscoupling of dipotassium salt of 2,2-(4-hydroxyphenyl)propane (43) with 1-bromonaphthalene (23).

The cation-radical polymerization of 2,2-bis[4-(1-naphthoxy)phenyl]propane (44) is presented in eq 31 from Scheme 11.11. The expected polymer structure is shown as structure 45 in this scheme. The results of the cation-radical polymerizations are summarized in Table 11.3. Experiment 1 (Table 11.3) was performed at FeCl₃/44 = 2.4 /1 (mol/mol) resulting in a 87% polymer yield. The molecular weight of the polymer was 4000 g/mol. An increase in the FeCl₃ concentration (experiment 2 versus 1) yielded both higher polymer yield and molecular weight. An increase of the monomer concentration (experiment 6 versus 2) also provided a slight increase of the molecular weight (4800 versus 4400 g/mol). Depending on the molecular weights of the polymers their glass transition temperatures (Tg) were in the range of 213 to 230 °C. The Tgs of the polymer
Scheme 11.10. Synthesis of 2,2-bis[4-(1-naphthoxy)phenyl]propane (44).
Scheme 11.11. Cation-radical polymerization of 2,2-bis[4-(1-naphthoxy)phenyl]propane (44).
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<th>Reaction</th>
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<td>FeCl₃ (mmol)</td>
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<td>Time (h)</td>
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Table 11.3. Polymerization of 2,2-Bis[4-(1-Naphthoxy)Phenyl]Propane (44).
derived from 44 with a 1,1-dinaphthyl group are significantly higher than that of the polyether containing a biphenyl group (166 °C).  

The polymerization of 2,2-bis[4-(1-naphthoxy)phenyl]propane (44) was followed at different polymerization times. Figure 11.6 presents the GPC traces of the polymers separated at various reaction times. Curve A represents the polymer obtained after 20 min. The $M_n$ of the sample was 2200 g/mol even though it contains a large amount of oligomers. This indicates that the polymerization of 44 is fairly fast. Curves B and C show the samples obtained at 2 h and 4 h respectively. Although a slight shift of the high molecular weight peak is noticeable, the $M_n$'s of the polymers were almost unchanged from that of curve A. This is due to the presence of a high amount of oligomers.

200 MHz $^1$H-NMR spectra of 2,2-bis[4-(1-naphthoxy)phenyl]propane (44) and of the polymer derived from 44 are presented in Figure 11.7 as spectra A and B respectively. The aliphatic region contains more resonances than expected for an ideal structure which corresponds to polymer 45 from Scheme 11.11. The expansions of the aliphatic regions of 44 and its corresponding polymer 45 are presented in Figure 11.8. The resonance of the methyl group from the isopropylidene unit in monomer 44 is observed at 1.69 ppm. The peak at 1.56 ppm is due to water. In spectrum B, three resonances are observed at 1.72, 1.39 and 1.13 ppm. The ratio of their respective integrals is 78 : 18 : 4. The resonance at 1.72 ppm corresponds to the methyl group of the isopropylidene unit of structure 45 from Scheme 11.11. The resonances at 1.39 and 1.13 ppm are assigned to the methyl groups in the 2-phenyl-2-naphthylpropane and 2,2-bis(naphthyl)propane units. These structural units are generated by the electrophilic transalkylation reactions.
Figure 11.6. GPC traces of polymers separated at different times of the polymerization of 2,2-bis[4-(1-naphthoxy)phenyl]propane (7) (experiments 3-5, Table 11.3): A) t = 20 min; B) t = 120 min; C) t = 240 min; all the samples were separated by precipitating the polymerization aliquot into methanol.
Figure 11.7. 200 MHz $^1$H-NMR spectra of 2,2-bis[4-(1-naphthoxy)phenylpropane] (7, spectrum A) and the polymer derived from 7 (spectrum B, sample from experiment 1, Table 11.3).
Figure 11.8. The expansion of 1-2 ppm of the 200 MHz $^1$H-NMR spectra of 2,2-bis[4-(1-naphthoxy)phenylpropane] (7, spectrum A) and the polymer derived from 7 (spectrum B, sample from experiment 1, Table 11.3).
It is known that under acidic conditions 2,2-bis(4-hydroxyphenyl)propane (42) undergoes transalkylation reactions with 2,6-dialkylphenol\(^{28}\) and with 2,6-diphenylphenol.\(^{29}\) Recently, the transalkylation reaction of 42 with diphenyl ether and with 4-bromophenyl phenyl ether were reported.\(^{30}\) When performed in the presence of strong protonic acids like triflic acid and Nafion resin these transalkylation reactions, generate intermediary monotransalkylated products and ditransalkylated products.\(^{28-30}\)

During the cation-radical polymerizations, no external protonic acid is added. Therefore, the transalkylation reactions are most probably catalyzed by the acid generated during the polymerization process. A mechanism for the transalkylation reaction occurring during the polymerization process is presented in Scheme 11.12 taking. The cation-radical polymerization proceeds through eqs 32 and 33 (Scheme 11.12). Two protons are released for each C-C coupling. Most of the hydrochloric acid formed is removed by continuous purging with nitrogen. However, some HCl is retained in the system most probably in the form of hydrogen irontetachloride, H\(^+\)[FeCl\(_4\)]\(^-\) which is a stronger acid than HCl (eq 34). The proton attacks the ipso position of the phenyl ring attached to the isopropylidene unit (eq 35) forming the \(\sigma\)-complex 48. The cleavage of 48 leads to the phenyl group 49 and carbocation 50 (eq 36). One possible reaction of 50 is the E1 elimination shown in eq 37. However, due to the permanent presence of protons in the reaction mixture 51 exists only in its protonated form 50. The carbocation 50 attacks the nucleophilic naphthoxy terminal unit of a monomer or a polymer 47 and generates the \(\sigma\)-complex of the naphthalene ring 52 (eq 38). Subsequent proton elimination leads to a monotransalkylated structural unit 53, i.e.
Scheme 11.12. Mechanism for the electrophilic transalkylation reaction of 2,2-bis[4-(1-naphthoxy)phenyl]propane (44) during the cation-radical polymerization.
Scheme 11.12 (Continued)
2-phenyl-2-naphthylpropane (eq 39). Structure 53 accounts for 18% of the total isopropylidene units available in the polymer.

The formation of the ditransalkylated structure is shown in eqs 40 to 44 from Scheme 11.12. It consists of the ipso protonation of the monotransalkylated structure 53 (eq 40) followed by subsequent cleavage to yield the naphthyl-carcocation 55 and the phenoxy terminated chain end 49 (eq 41). The attack of carbocation 55 on the terminal naphthoxy unit 47 (eq 42) followed by proton elimination (eq 43) generates the ditransalkylated structure 57. This type of structural units represents only 4% of the isopropylidene units of the polymer. This is an expected result since for nucleophilicity reasons the ipso attack from eq 38 takes place mostly on the naphthalene ring and therefore, generating a carbocation similar to 52 from eq 44.

The total amount of transalkylated isopropylidenic units represents up to 22% of all the structural units of the polymers. Therefore, the transalkylation reaction represents a significant process during the cation-radical polymerization of 2,2-bis[4-(1-naphthoxy)phenyl]propane (44).

The low molecular weights of the polymers derived from 44 are caused by the generation of phenoxy chain ends 49 produced during the transalkylation reactions. It has been demonstrated that the bis(phenoxy) groups have a low polymerizability under cation-radical conditions and thus lead only to oligomers (Chapter 6). At the same time due to their lower nucleophilicity and therefore the reactivity even during the transalkylation steps they are less reactive than the naphthoxy groups. Based on this discussion, the structure of the polymers obtained from monomer 44 is most probably similar to that of 58 from Scheme 11.12.
11.4. CONCLUSIONS

The synthesis and polymerization of 4,4'-bis(1-naphthoxy)biphenyl (12), 2,2'-bis(1-naphthoxy)biphenyl (13), 3,3'-bis(1-naphthoxy)biphenyl (19), and 1,3-bis(1-naphthoxy)benzene (24) have demonstrated that the cation-radical polymerization of bis(1-naphthoxy)aryls represents a general method for the synthesis of fully aromatic polyethers. 2,2-bis[4-(1-naphthoxy)phenyl]propane (44) polymerizes by two different propagation steps. The first one represents a cation-radical dimerization of the naphthyl groups to dinaphthyl structure. H+FeCl4- generated from the first propagation step initiates a transalkylation reaction which provides structural units containing isopropylidenic groups inserted between phenyl and naphthyl, and between two naphthyl groups respectively. Since the phenyl groups resulted from the second propagation reaction are unreactive in both the oxidative coupling and the transalkylation steps this polymerization reaction leads to polymers with low molecular weights containing phenyl chain ends.

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PART III
REACTIVITY OF PPO-VBE
MACROMONOMERS
CHAPTER 12

REACTIVITY of \( \omega-(p\text{-VINYLBENZYLETHER}) \)
MACROMONOMER OF
POLY(2,6-DIMETHYL-1,4-PHENYLENE OXIDE)

12.1. INTRODUCTION

The copolymerization of a macromonomer of narrow molecular weight distribution with a low molecular weight monomer represents the "state-of-the-art" approach to the synthesis of well-defined graft copolymers.\(^1\text{-}^6\) However, the composition and sequence distribution of graft copolymers is determined by both comonomer feed composition and by the reactivity of the macromonomer. At the present, there is very little understanding of the reactivity of macromonomer.\(^1\text{-}^6\)

The reactivity of macromonomers should be molecular weight independent. However, several research groups have reported results which demonstrate that the reactivity of macromonomers is molecular weight dependent,\(^7\text{-}^{12}\) and even conversion dependent\(^8\). The dependence of macromonomer reactivity on molecular weight has been interpreted in terms of kinetic excluded volume effects,\(^9\text{-}^{11}\) thermodynamic repulsive interactions,\(^9\text{-}^{12}\) and the onset of microphase separation.\(^8\) However, the actual mechanism which provides these results is still open to debate.

According to the terminal model of binary copolymerization, for the case of radical copolymerization the reactivity ratios should be independent of the nature of copolymerization solvent, total monomer concentration, and nature and concentration of the radical initiator used.\(^13\) This certainly assumes that the
copolymerization takes place in an ideal solution and therefore, reactivity ratios are only temperature dependent.

Nevertheless, there are numerous examples of polar monomer pairs of which reactivity ratios were reported to be dependent on the nature of the solvent used in copolymerization. This may imply that the terminal mechanism of copolymerization is not valid for the case of these monomer pairs. Alternatively, these results may represent experimental artifacts which are provided by the nonideality of the copolymerization solution. Recently, Harwood et al. have reinvestigated a number of these copolymerization systems and have demonstrated that the sequence distributions of the copolymers at the same composition are identical for copolymers synthesized from different solvents. This means, these monomer pairs obey the same copolymerization mechanism, i.e. have the same reactivity ratios in different solvents. Nevertheless, the nature of the copolymerization solvent provides around the growing chains monomer compositions which are different from those used in the initial reaction mixture. Therefore, the comonomers composition around the growing chain being different from that used in the calculation of reactivity ratios provides the experimental artifacts observed in the determination of reactivity ratios. The concept that a growing active chain can control its own environment during copolymerization was named the "bootstrap model" and its implications were recently reviewed.

In going from a pair of monomers to the corresponding homopolymers, the solubility between the two compounds differs to the point that while the monomers were purely insoluble, the polymers are completely immiscible. Therefore, a pair of monomers which was not enough dissimilar in polarity to provide solvents effects on their reactivity ratios, might give this artifacts when at least one of the two
monomers becomes a macromonomer. Due to the dissimilarity between the affinity of the free and grafted macromonomer and backbone segments to solvent-low molecular weight monomer mixture, we can assume that similar concentration partitions like in the "bootstrap model" may occur during the copolymerization of monomer-macromonomer pairs. These effects can be detected by performing copolymerization experiments at different total monomer concentrations and in different solvents.

The goal of this chapter is to investigate the influence of total monomer concentration and of different solvents, on the reactivity of poly(2,6-dimethyl-1,4-phenylene oxide)-ω-(p-vinylbenzyl ether) (PPO-VBE) with two molecular weights. The reactivity of PPO-VBE was determined from radical copolymerization experiments using methyl methacrylate (MMA) as comonomer.

12.2. EXPERIMENTAL

12.2.1. Materials

4-bromo-2,6-dimethylphenol (Aldrich) was purified by recrystallization from petroleum ether. p-Chloromethylstyrene (Seimi Chemical, Kanagawa, Japan) was used as received. Methyl methacrylate (MMA, M₁) (Aldrich) was first washed with 10% NaOH aqueous solution to remove the inhibitor, then washed with distilled water, dried over anhydrous CaCl₂, and distilled under vacuum. Tetrabutylammonium hydrogen sulfate (TBAH) (Aldrich) was used as received. α,α'-Azobisisobutyronitrile (AIBN) (Fluka) was freshly recrystallized from methanol at temperature below 40°C. Toluene, chlorobenzene, and 1,2-dichlorobenzene were washed with dilute sulfuric acid to remove thiophene and olefines, then washed with distilled water, dried over anhydrous CaCl₂, and then
distilled from sodium. Benzene was washed the same way as for toluene, and distilled from CaH₂. Tetrahydrofuran (THF) was distilled from LiAlH₄.

12.2.2. Techniques

GPC analyses were carried out with a Perkin-Elmer series 10 LC instrument equipped with LC-100 column oven, LC 600 autosampler, and a Nelson interface networked with a personal computer. The measurements were made using a UV detector set at 254 nm, THF as solvent (1ml/min, 40°C), a set of PL-gel columns of 10², 5 X 10², 10³, 10⁴, and 10⁵ Å, and a calibration curve constructed with polystyrene standards (Supelco). Gas chromatographic analyses were performed with a Hewlett Packard HP 5890A gas chromatograph equipped with a HP 3392A integrator and SP 1000 column (carbowax 20 and terephthalic acid derivative) from Supelco. For polymerization samples in benzene, toluene and THF the temperatures of the oven, injector and detector were 110 °C, 150 °C and 150 °C. For reactions performed in chlorobenzene these temperatures were 130 °C, 160 °C and 160 °C, while for those performed in 1,2-dichlorobenzene they were 180 °C, 190 °C and 210 °C. 200 MHz ¹H-NMR spectra were recorded on a Varian XL-200 spectrometer. All the spectra were obtained at 55 °C with TMS as the internal standards.

12.2.3. Synthesis of PPO-VBE Macromonomers.

The syntheses of PPO-OH and PPO-VBE were performed as previously described (Scheme 12.1).¹¹,¹⁶ The obtained PPO-VBE has \( M_n = 6,900; M_w/M_n = 1.91 \). A series of PPO-VBE macromonomers with different molecular weights and narrow polydispersities were obtained by a modified fractionation scheme from
previously detailed procedure (Scheme 12.2). Two PPO-VBE fractions were used for concentration effects studies; one with $\overline{M}_n = 15,200$ and $\overline{M}_w/\overline{M}_n = 1.22$, and the other with $\overline{M}_n = 5,100$ and $\overline{M}_w/\overline{M}_n = 1.26$. The PPO-VBE macromonomer used for solvent effects has $\overline{M}_n = 12,900$ and $\overline{M}_w/\overline{M}_n = 1.18$. The number average molecular weights and polydispersities were determined by GPC with polystyrene standards. The number average molecular weights of PPO-VBE macromonomers lower than 15,000 agree unexpectedly well with those determined by VPO.

12.2.4. Free Radical Copolymerization of PPO-VBE with MMA

The copolymerization ingredients were weighed into a polymerization tube as previously described in detail.\textsuperscript{11} The tube was sealed and degassed by at least five freeze-thaw cycles on a high vacuum line. The tube was then filled with dry high purity nitrogen or argon and heated in an oil bath at 60°C. The conversion of both monomer and macromonomer were followed by taking samples at various polymerization times with a syringe, which was simultaneously flushed with a stream of inert gas to prevent air contamination. Solution of 0.2 mL was withdrawn. The solutions were precipitated into methanol for polymerizations using benzene, toluene, chlorobenzene and 1,2-dichlorobenzene as solvents, whereas n-hexane was used for polymerizations performed in THF. The conversion of unreacted macromonomer was determined by GPC with a UV detector set at 254 nm. Since PMMA does not absorb UV at this wavelength, the ratio of the area under the GPC trace of the macromonomer and the graft copolymer, therefore, equals the ratio of unpolymerized macromonomer and macromonomer that was incorporated into the graft copolymer, respectively.

The conversion of unreacted MMA was determined by GC using the
Scheme 12.2. Fractionation of PPO-VBE macromonomers.
polymerization solvents as an internal standard. The reactivity ratio of MMA ($r_1$) was determined as the slope of the -$\log [M_1]/[M_1]_0$ versus -$\log [M_2]/[M_2]_0$ plot; i.e. by using Jaacks integrated copolymerization equation:

$$- \log \frac{[M_1]_t}{[M_1]_0} = - \log \frac{[M_2]_t}{[M_2]_0}$$

12.3. RESULTS AND DISCUSSION

12.3.1. Influence of the Macromonomer Concentration on the Reactivity of PPO-VBE Macromonomers

The free radical copolymerization of PPO-VBE macromonomer with methyl methacrylate is presented in Scheme 12.3. The reactivity ratio of methyl methacrylate ($M_1$), $r_1$, was determined as the slope of the -$\log [M_1]/[M_1]_0$ versus -$\log [M_2]/[M_2]_0$ plot. This method was previously described and discussed in detail. For PPO-VBE ($M_2$) with $\overline{M}_n = 15,200$ and $\overline{M}_w/\overline{M}_n = 1.22$, $r_1$ was determined at different total monomer concentrations. The obtained results are summarized in Table 12.1. The copolymerization experiments were designed so that $[M_1]/[M_2]$ was maintained constant in all the experiments. Only the amount of solvent was varied, to give a range of macromonomer concentrations from $3.754 \times 10^{-3}$ mol/l (experiment 1 in Table 12.1) to $11.240 \times 10^{-3}$ mol/l (experiment 7 in Table 12.1). The sequence length of MMA monomer units in graft copolymer, assuming only one PPO graft per graft copolymer, $n_1$, was calculated based on the $M_n$ of the resulting graft copolymer determined from GPC measurements. Except for the copolymerization experiment performed with the lowest $[M_2]$ concentration (experiment 1 from Table 12.1) all other graft copolymers have incorporated more MMA structural units than the theoretical $n_1$, i.e. $n_1' > n_1$. This result demonstrates
Scheme 12.3. Free radical copolymerization of PPO-VBE macromonomer with methyl methacrylate (MMA).

Polymerization solvents: Toluene, Benzene, Chlorobenzene, o-Dichlorobenzene, and Tetrahydrofuran.
Table 12.1

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<td>0.0024</td>
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<td>0.0024</td>
<td>0.0024</td>
</tr>
<tr>
<td>6</td>
<td>2.0000</td>
<td>0.0500</td>
<td>0.0024</td>
<td>50</td>
<td>6.754</td>
<td>3.754</td>
<td>2.0000</td>
<td>0.0500</td>
<td>0.0024</td>
<td>0.0024</td>
<td>0.0024</td>
<td>0.0024</td>
<td>0.0024</td>
<td>0.0024</td>
</tr>
<tr>
<td>7</td>
<td>2.0000</td>
<td>0.0500</td>
<td>0.0024</td>
<td>50</td>
<td>6.754</td>
<td>3.754</td>
<td>2.0000</td>
<td>0.0500</td>
<td>0.0024</td>
<td>0.0024</td>
<td>0.0024</td>
<td>0.0024</td>
<td>0.0024</td>
<td>0.0024</td>
</tr>
</tbody>
</table>

*M1 and M2 [M1] and [M2] are the molecuar weights of MMA and M2, respectively.

\(n_i\) of repeat unit is not meaningful here since in most cases \(n_i > 1\).

\(\alpha_{i}^{n}\) is not meaningful here since in most cases \(n_i > 1\).
that the values of \( r_1 \) are meaningful, i.e. that the resulting graft copolymer contains at least one PPO.

The variation of \( r_1 \) as a function of [M\(_2\)] is plotted in Figure 12.1 as curve A. These results have shown that the determined \( r_1 \) decreases with the increase in [M\(_2\)]. This dependence is unexpected for a binary copolymerization system which follows the terminal model of copolymerization.

A macromonomer with a lower molecular weight (\( \bar{M}_n = 5,100; \frac{M_w}{M_n} = 1.26 \)) was used to investigate whether its reactivity is concentration dependent as in the case of the macromonomer with high \( M_n \). The experimental results are listed in Table 12.2 and plotted as curve B in Figure 12.1. However, the determined \( r_1 \) values are higher than any of those obtained for the PPO-VBE macromonomers with different molecular weight.\(^{11}\) A closer examination of the \( M_n \) of the graft copolymers demonstrates that they are lower than the molecular weights corresponding to one structural unit of the graft copolymer. The graft copolymer should have a higher molecular weight than that obtained by using calibration based on linear polystyrene standards. However, the relatively low ratio of PPO graft to PMMA backbone units (one PPO graft for about 500 MMA monomer units) makes the requested correction be very small. Assuming that the \( M_n \) from GPC determination is acceptable, the actual MMA sequence length is only 60 to 70 % of the values which can provide reliable \( r_1 \) values. The \( r_1 \) values (\( r_1' \)) were calculated from \( n_1' \) data. These \( r_1' \) values are in the range expected.\(^{11}\) These corrected \( r_1' \)s are plotted as curve C in Figure 12.1. The \( r_1' \) values as the \( r_1 \) values for this molecular weight of the macromonomer are relatively independent of the overall concentration of the macromonomer, the general trend is a slight decrease of \( r_1 \) with the increase in [M\(_2\)].
Figure 12.1. The dependence of $r_1$ on the concentration of PPO-VBE macromonomer [M$_2$] in the monomer feed. A) $\overline{M}_n$ = 15,200; $\overline{M}_w/\overline{M}_n$ = 1.22, B) $\overline{M}_n$ = 5,100; $\overline{M}_w/\overline{M}_n$ = 1.26, experimental; C) $\overline{M}_n$ = 5,100; $\overline{M}_w/\overline{M}_n$ = 1.26, corrected.
Table 12.2

The Influence of Macromonomer Concentration on the $r_i$ Determined from the Radical Copolymerization of MMA ($M_1$) with PPO-VHE ($M_2$, $M_n^P$ = 5100; $M_w/M_n$ = 1.20); Polymerization Solvent, Toluene; Polymerization Temperature, 60°C; Initiator, AIBN

<table>
<thead>
<tr>
<th>Experiment no.</th>
<th>$M_1$</th>
<th>$M_2$</th>
<th>AIBN</th>
<th>Toluene</th>
<th>$[M_1]/[M_2]$</th>
<th>$[M_2]$</th>
<th>$r_i$</th>
<th>$\frac{n_i}{[M_1]}$</th>
<th>$\frac{n_i}{[M_2]}$</th>
<th>$\bar{M}_n$ (g/mol) of graft copolymer (by GPC)</th>
<th>$\bar{M}_g$ (g/mol)</th>
<th>$n_i^c$</th>
<th>$n_i^d$</th>
<th>$r_i^c$</th>
<th>$r_i^d$</th>
<th>$r_i^{a}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>1.005</td>
<td>0.107</td>
<td>55</td>
<td>6.813</td>
<td>477</td>
<td>2.671</td>
<td>1.086</td>
<td>519</td>
<td>41,500</td>
<td>57,100</td>
<td>308</td>
<td>0.769</td>
<td>71</td>
<td>0.789</td>
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</tr>
<tr>
<td>2</td>
<td>2.021</td>
<td>0.199</td>
<td>20</td>
<td>9.649</td>
<td>518</td>
<td>3.495</td>
<td>1.060</td>
<td>550</td>
<td>41,100</td>
<td>56,200</td>
<td>360</td>
<td>0.693</td>
<td>65</td>
<td>0.767</td>
<td></td>
<td></td>
</tr>
<tr>
<td>3</td>
<td>2.019</td>
<td>0.203</td>
<td>22</td>
<td>7.285</td>
<td>507</td>
<td>4.724</td>
<td>1.096</td>
<td>557</td>
<td>45,000</td>
<td>60,900</td>
<td>390</td>
<td>0.765</td>
<td>72</td>
<td>0.785</td>
<td></td>
<td></td>
</tr>
<tr>
<td>4</td>
<td>2.015</td>
<td>0.208</td>
<td>21</td>
<td>5.900</td>
<td>491</td>
<td>6.017</td>
<td>1.125</td>
<td>553</td>
<td>42,900</td>
<td>60,500</td>
<td>378</td>
<td>0.768</td>
<td>68</td>
<td>0.813</td>
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<td></td>
</tr>
<tr>
<td>5</td>
<td>1.014</td>
<td>0.107</td>
<td>24</td>
<td>2.350</td>
<td>498</td>
<td>7.709</td>
<td>1.092</td>
<td>527</td>
<td>39,700</td>
<td>57,300</td>
<td>346</td>
<td>0.693</td>
<td>66</td>
<td>0.756</td>
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<td></td>
</tr>
</tbody>
</table>

*M_1 = molecular weight of MMA; $\bar{M}_g$ (2) = $\bar{M}_n$ of $M_2$.

$n_i^c = \frac{\bar{M}_g (\text{graft copolymer}) - \bar{M}_g (2)}{M_i}$, i.e., it is assumed that the graft copolymer contains only one repeat unit.

$r_i^c = (n_i^c - 1) \frac{[M_1]}{[M_2]}$.

$r_i^{a}$ (corrected) = $r_i^c \times \frac{n_i^c (\text{exp. no. 3})}{n_i^c}$, i.e., $r_i^{a}$ is compared to the $r_i^c$ corresponding to the highest $n_i^c$. 
12.3.2. The Influence of the Nature of Polymerization Solvent on the Reactivity of PPO-VBE Macromonomers

The copolymerization of the PPO-VBE macromonomer was also conducted in several different solvents. The concentration \([M_2]\) was maintained constant. The experimental results are presented in Table 12.3. The determined \(r_1\)'s were found to depend on the nature of the polymerization solvent. This kind of solvent effect on the reactivity ratios has been observed by different investigators and discussed by Harwood\(^{15}\) for several pairs of monomers of different polarities. Harwood proposed the so-called "Bootstrap model" to account for such profound solvent effects on the reactivity ratios. From the above concentration and solvent effects, it appears that the bootstrap model applies to macromonomer-monomer copolymerization systems.

12.3.3. The Interpretation of the Concentration and Solvent Effects

When copolymerization was performed in toluene, toluene was a better solvent for PPO than for PMMA. This difference in the affinity of the two types of polymer growing chain segments with solvent create a partition of PPO-VBE (M2) macromonomer and MMA between the bulk of free solvent and around the growing chain. The growing radical is best represented as a reversed micelle type entity with PPO graft outsied-pointed to the solvent (toluene) rich direction (Figure 12.2). The concentrations of \(M_1\) and \(M_2\) are no more uniform throughout the solution but are variable and depend upon the location in question. This type of concentration nonideality is best respsented by a partition coefficient similar to that proposed by Harwood\(^{11}\):
Table 12.3

The Influence of Copolymerization Solvent on the \( r_1 \) Determined from the Radical Copolymerization of MMA (\( M_1 \)) with PPO–VBE (\( M_2 \), \( M_n = 12,000 \); \( \bar{M}_n/\bar{M}_w = 1.18 \)); Polymerization Temperature, 60°C; Initiator, AIBN

<table>
<thead>
<tr>
<th>Experiment no.</th>
<th>Polymerization solvent</th>
<th>( M_1 ) (g)</th>
<th>( M_2 ) (g)</th>
<th>AIBN (mg)</th>
<th>Solvent ( [M_1]/[M_2] ) (mol/mol)</th>
<th>( [M_2] ) (( \times 10^4 ) mol/L)</th>
<th>( r_1 \left( \frac{[M_1]}{[M_2]} + 1 \right) )</th>
<th>( \bar{M}_n ) (g/mol) of graft copolymer (by GPC)</th>
<th>Calculated ( \bar{M}_n ) of graft copolymer repeat unit (g/mol)</th>
<th>( \bar{M}_n/(2+M_1\times n_1) \times 10^4 )</th>
<th>( n_1^n )</th>
<th>( n_1^b )</th>
<th>( r_1^c )</th>
<th>( \times 100 )</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>Toluene</td>
<td>1.023</td>
<td>0.301</td>
<td>50</td>
<td>3.933</td>
<td>438</td>
<td>5.143</td>
<td>0.800</td>
<td>351</td>
<td>44,700</td>
<td>48,000</td>
<td>318</td>
<td>0.724</td>
<td>91</td>
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<tr>
<td>2</td>
<td>Benzene</td>
<td>1.028</td>
<td>0.295</td>
<td>18</td>
<td>3.939</td>
<td>449</td>
<td>5.065</td>
<td>0.883</td>
<td>442</td>
<td>77,800</td>
<td>57,100</td>
<td>649</td>
<td>1.443</td>
<td>147</td>
</tr>
<tr>
<td>3</td>
<td>Chloro-benzene</td>
<td>1.028</td>
<td>0.302</td>
<td>19</td>
<td>5.022</td>
<td>438</td>
<td>5.146</td>
<td>1.075</td>
<td>472</td>
<td>81,300</td>
<td>60,100</td>
<td>684</td>
<td>1.559</td>
<td>145</td>
</tr>
<tr>
<td>4</td>
<td>THF</td>
<td>1.024</td>
<td>0.317</td>
<td>22</td>
<td>3.965</td>
<td>417</td>
<td>5.491</td>
<td>0.903</td>
<td>378</td>
<td>45,800</td>
<td>50,700</td>
<td>329</td>
<td>0.968</td>
<td>87</td>
</tr>
<tr>
<td>5</td>
<td>Dichloro-benzene</td>
<td>1.029</td>
<td>0.300</td>
<td>23</td>
<td>5.922</td>
<td>442</td>
<td>5.128</td>
<td>0.798</td>
<td>353</td>
<td>91,500</td>
<td>57,100</td>
<td>786</td>
<td>2.224</td>
<td>223</td>
</tr>
</tbody>
</table>

*\( M_1 \) = Molecular weight of MMA; \( \bar{M}_n/(2+M_1\times n_1) \) of PPO–VBE.

\( \bar{M}_n/(2+M_1\times n_1) \times 10^4 \).

\( r_1 = (n_1^n - 1)/([M_1]/[M_2]) \); \( r_1^c \) is not meaningful here since in most cases \( n_1^n > n_1 \).
Figure 12.2. Schematic representation of monomer concentration partition between growing chain and bulk of free solvent during polymerization.
\[ k = \frac{[M_1]_{\text{chain}}/[M_2]_{\text{bulk}}}{[M_2]_{\text{chain}}/[M_1]_{\text{bulk}}} = \frac{[M_1]_{\text{chain}}/[M_2]_{\text{chain}}}{[M_1]_{\text{bulk}}/[M_2]_{\text{bulk}}} \]

The Jaacks' differential equation:

\[ \frac{d[M_1]}{d[M_2]} = r_1 \frac{[M_1]}{[M_1]} \]

should be considered in the following form:

\[ \frac{d[M_1]}{d[M_2]} = r_1^0 \frac{[M_1]_{\text{chain}}}{[M_1]_{\text{chain}}} = (r_1^0 \times k) \frac{[M_1]_{\text{bulk}}}{[M_1]_{\text{bulk}}} \]

\[ r_1 = r_1^0 \times k \]

Where \([M_1]\) = average concentration of \(M_1\).

\([M2]\) = average concentration of \(M_2\).

\(r_1^0\) = true \(r_1\) from terminal model and should be constant, i.e. independent of macromonomer molecular weight, macromonomer concentration and polymerization solvent.

The experimentally determined and used monomer concentration is the averaged concentration between bulk and around the growing chain. The determined \(r_1\) is a composite product of the true \(r_1\) (i.e. \(r_1^0\)) and the partition coefficient. The physical picture is that \([M_1]\) is enhanced in the interior of the micelle, while PPO-VBE macromonomer concentration ([M_2]) is higher close to the outside-pointed PPO grafts. The present experiments provided \(r_1\) larger than \(r_1 = 0.656\) which corresponds to the \(r_1\) for PPO-VBE with \(M_n = 2,380\) macromonomer.\textsuperscript{11} This indicates that \(k > 1\), i.e. \([M_1]_{\text{chain}}/[M_1]_{\text{bulk}} > [M_2]_{\text{chain}}/[M_2]_{\text{bulk}}\) as determined by the much larger number of MMA units incorporation into the graft copolymer system. Also, due to \([M_1] >> [M_2]\); as
previously discussed, the micelle formation arises from the much higher affinity of PPO grafts towards solvent (toluene) molecules. Therefore, it is natural that the macromonomer concentration controls the extent of micelle formation, i.e. $k$ is determined primarily by $[M_2]_{\text{chain}}/[M_2]_{\text{bulk}}$. As $[M_2]$ increases, the extent of micelle formation and accordingly the extent of partition increases, which implies that $[M_2]_{\text{chain}}/[M_2]_{\text{bulk}}$ increases with $[M_2]$. Therefore $r_1$ is consequently decreased since $r_{10}$ is constant as assumed by terminal model of copolymerization.

For different solvents, due to the different affinities towards PPO grafts, the partition coefficients should also be expected to different even at the same concentration (Table 12.3).

In order to verify the proposed micelle hypothesis, one graft copolymer (from experiment 4 in Table 12.1) was selected to run 200 MHz $^1$H-NMR experiments in different deuterated solvent mixtures which may resemble the polymerization medium. The first series of experiments were performed in mixtures of CDCl$_3$ and CD$_3$COCD$_3$ since acetone resembles the solubility behavior of MMA. Representative $^1$H-NMR spectra are presented in Figure 12.3. Chloroform is a good solvent for both PPO and PMMA, and therefore, an ideal random polymer chain distribution is expected for chloroform solution. Acetone is a good solvent for PMMA only. As the volume of acetone in the solvent mixture is increased, the integral of the aromatic region derived from PPO grafts decreases. The phenyl peak disappears completely at CDCl$_3$/CD$_3$COCD$_3$ = 1/5 (v/v). The decrease of the ratio of integrals I (phenyl from PPO graft) to I(MeO from PMMA backbone) is plotted as the solvent composition in Figure 12.4. This phenomenon can be easily interpreted in terms of micelle formation as pictured in Figure 12.5.
Figure 12.3. 200 MHz $^1$H-NMR spectra of PMMA-g-PPO graft copolymer (polymer from experiment 4 in Table 12.1) in different ratios of CDCl$_3$ to CD$_3$COCD$_3$ (v/v) (55°C).
Figure 12.4. The dependence of $I$(phenyl)/(in the PPO grafts)/$I$(MeO) (in PMMA backbone on the solvent compositions (CDCl$_3$/CD$_3$COCD$_3$) (v/v).
Figure 12.5. Schematic representation of micelle formation of PMMA-g-PPO in the mixtures of CDCl₃/CD₃COCD₃ solvents.
As long as the monomers partition exists, the accurate determination of reactivity of macromonomer is impossible. Low macromonomer concentration in the initial monomer feed far below critical micelle concentration (CMC) would theoretically reduce such artifacts. But, at low monomer concentrations, the molecular weight of graft copolymer is lower and the poor separation of polymer from unreacted macromonomer on GPC instrument makes the conversion determinations as required for kinetic experiments less accurate.

12.4. CONCLUSIONS

The determined reactivity ratios \( r_1 \) decreases with the increase in macromonomer concentration. The nature of polymerization solvent affects the reactivity ratios determined. Micelle formation was demonstrated by \(^1\text{H}-\text{NMR} \) spectroscopy performed in different solvent mixtures. Monomer partition between the bulk of solvent and around growing chain can be used to account for the observed concentration and solvent effects. The determination of the absolute reactivity ratios requires quantitative determination of the sequence length \( n_1 \) and \( n_2 \).

REFERENCES


GENERAL CONCLUSIONS

Part I. Anion-Radical Synthesis of Poly(2,6-Dimethyl-1,4-Phenylene Oxide)s

Several novel synthetic approaches have been developed to synthesize poly(2,6-dimethyl-1,4-phenylene oxide)s (PPO) with controlled functionalities and molecular weights. The accomplishments consist of the phase transfer catalyzed (PTC) anion-radical copolymerization of 4-bromo-2,6-dimethylphenol (BDMP) with various comonomeric phenols. These developments offer convenient and efficient synthesis of PPO precursors for both macromonomers and telechelics.

The PTC copolymerization of BDMP with either 2,4,6-trimethylphenol (TMP) or 4-tert-butyl-2,6-dimethylphenol (TBDMP) leads to the PPO with one 2,6-dimethylphenol chain end (PPO-OH). The molecular weights of the resulting polymers is controlled by the molar ratios of either BDMP/TMP or BDMP/TBDMP. The PPO-OH synthesized from BDMP/TMP has benzyl ether structural units resulted from the α-proton abstraction of the 4-methyl group of TMP. The polymers synthesized at high molar ratios of BDMP/TMP have a bimodal molecular weight distribution caused by the two types of propagating phenoxy radicals of different reactivities. The polymers synthesized from BDMP/TBDMP have a monomodal molecular weight distribution and narrow polydispersity. Therefore, the PPO-OH polymers synthesized by the BDMP/TBDMP method are ideal precursors for macromonomers.

The PTC copolymerization of BDMP with bifunctional initiating phenols, i.e. 2,2-bis(4-hydroxy-3,5-dimethylphenyl)propane yields telechelic PPO containing two 2,6-dimethylphenol chain ends (PPO-2OH). The PTC
copolymerization of BDMP with 4-hydroxy-3,5-dimethylbenzyl alcohol produced a mixture of PPO-OH and PPO-2OH.

The PTC copolymerization with 4-substituted 2,6-di-tert-butylphenol produced PPO chain ended with the terminating phenols. The phenol with 4-bromo group is more efficient than the phenol with 4-tert-butyl group due to both the reduced steric hindrance and the subsequent easy elimination of bromide. The molecular weight of PPO synthesized by this method is controlled by the molar ratio of BDMP to the terminating phenol.

PTC depolymerization of high molecular weight PPO-OH, in the presence of either TMP or TBDMP and air, proceeds by an anion-radical mechanism. These depolymerization reactions led to PPO-OH with similar structure with those resulted from the polymerization of BDMP.

Part II. Cation-Radical Synthesis of Aromatic Polyethers

Cation-radical polymerization of 4,4'-bis(phenoxy)diphenyl sulfone, its substituted derivatives, and 4,4'-bis(phenylthio)diphenyl sulfone produced poly(ether sulfone)s of low molecular weights. The low polymerizability of the monomers is determined by low oxidizability of the phenoxy, substituted phenoxy and phenylthio aromatic rings. The increase in the polymerizability from the phenoxy to the phenylthio, and from phenoxy to phenoxy substituted with various electron-donating substituents suggest that the overall polymerizability of these monomers is determined by the oxidizability of the monomers.

The cation-radical polymerization of 1,5-bis(phenoxy)pentane, 1,5-bis(phenoxy)pentanes substituted with various electron-donating groups, and 1,5-bis(phenylthio)pentane indicates the low polymerizability of the monomers. While
the overall oxidizability of these monomers is still low (as indicated by both the low polymer yields and the low molecular weights of polymers), the cation-radical generated by the single electron oxidation is stabilized by the oxonium cation-radical species. Only the non-oxonium cation-radical is capable of C-C coupling, but it exists only in low concentration. The low reactivity of the cation-radical is further demonstrated by the extensive proton transfer reactions of the methyl substituted monomers.

A comparison between the first two classes of monomers suggests that the monomers containing diphenyl sulfone linkage have a higher polymerizability. This is determined by the reactivity of the cation-radical species. The proton transfer was observed in only one of the methyl substituted monomers with diphenyl sulfone linkage. However, all the methyl substituted monomers with pentoxy linkage undergo the proton transfer reactions. This implies that the proton transfer reaction depends on the reactivity of the cation-radicals. More reactive cation-radicals (with diphenyl sulfone linkage) are less prone to the proton transfer reactions.

A critical comparison of 4,4'-bis(1-naphthoxy)diphenyl sulfone and 1,5-bis(1-naphthoxy)pentane reveals that the overall polymerizability between these two monomers is dominated by the reactivity of the cation-radical species. The cation-radical derived from 1,5-bis(1-naphthoxy)pentane is stabilized by its oxonium isomer and is therefore less reactive.

The reactivity of the monomers in the cation-radical polymerization was further demonstrated by the cation-radical copolymerization of α,ω-[4-(1-naphthoxy)phenylsulfonyl]perfluoroalkanes with 1,5-bis(1-naphthoxy)pentane. As
predicted by the copolymerization equation, copolymers with higher content of the more reactive comonomer were obtained.

The example in which the overall polymerizability of a pair of bis(1-naphthoxy) monomers dominated by the reactivity of the monomers is provided by the monomers containing either two carbonyl groups or two methylene groups. The electron-donating capability of the methylene groups is responsible for the higher polymerizability of the monomers with two CH₂ groups than those with two carbonyl groups.

The bis(phenoxy) and bis(phenylthio) monomers exhibit a much lower polymerizability than the corresponding bis(1-naphthoxy) monomers. Under the same oxidation polymerization conditions, this difference leads to higher molecular weight polymers for the bis(1-naphthoxy) monomers than the bis(phenoxy) and bis(phenylthio) monomers.

The synthesis of fully aromatic polyethers by Scholl reaction has demonstrated that the cation-radical polymerization is a general synthetic route to the synthesis of aromatic polyethers either with or without functional groups. Functional groups other than sulfonyl, carbonyl, or perfluoroalkylsulfonyl groups can be inserted between the reactive bis(1-naphthoxy) aromatic groups.

In conclusion, the polymerizability of a pair of monomers can be determined by either the reactivity of the monomers or the reactivity of the cation-radical growing species depending on the structure of the monomers.

Part III. The Reactivity of PPO-VBE Macromonomers

The determined "reactivity" of PPO-VBE macromonomers by free radical copolymerization is influenced by the molecular weights of the macromonomers,
by the macromonomer concentration, and by the nature of the polymerization solvents. The copolymerization is heterogeneous due to the micelle formation. The comonomer concentrations are partitioned between the bulk of the solvent and around the growing chain. Therefore, the determined reactivity of the macromonomer does not represent the actual reactivity, therefore the non-ideal nature of the macromonomer-low molecular weight comonomer copolymerization should be carefully considered. The design of well-defined graft copolymer architecture should be based on results from both the determined reactivity and the direct measurement of the sequence length distribution of the graft copolymers.
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Chapter 1


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Chapter 2


**Chapter 3**


Chapter 4


Chapter 5


Chapter 6


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Chapter 9


Chapter 10


Chapter 11


Chapter 12


