Modified Poly(2,6-dimethyl-1,4-phenylene ether)s Prepared by Redistribution

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ABSTRACT: Redistribution of poly(2,6-dimethyl-1,4-phenylene ether) (PPE) with a phenolic compound yields a depolymerized polymer having the phenolic compound incorporated as the tail end. The molecular weight of the product is adjusted by use of the ratio of phenol over PPE repeating units. PPE oligomers and telechelics with a large variety of end groups, including reactive end groups, can be prepared in this way. Furthermore, block copolymers can be prepared by reacting a phenol terminated polymer in a redistribution with PPE. This is illustrated by the reaction of phenol terminated polystyrene with PPE, leading to polystyrene–PPE diblock copolymers. TMDPQ or copper/amine catalysts can be used as catalyst depending on the reaction phenolic compound, desired reaction time, and product purity. For a fast PPE redistribution with ortho-unsubstituted phenols, without any oxidation of the methyl substituents of the PPE chain, the use of TMDPQ is preferred. For the preparation of pure oligomers and block copolymers, a slow redistribution using copper catalysts in the absence of oxygen is preferred.

Introduction

The conventional synthesis of poly(2,6-dimethyl-1,4-phenylene ether) (PPE) is based on the oxidative coupling mechanism of 2,6-dimethylphenol (DMP) as discovered by Hay.1–5 It is well-known that during the oxidative coupling polymerization of DMP, redistribution reactions simultaneously occur. The most widely accepted mechanism6–11 for these reactions is based on phenoxy radicals, as outlined in Figures 1 and 2. Chain elongation is the result of coupling of these radicals via the formation of a quinol ether on the free para-position of a tail-end or monomer phenol ring, whereas redistribution involves a coupling to a quinone ketal on the para-position of a headgroup phenol ring. This ketal unit can either dissociate or undergo an intramolecular rearrangement,9,12–14 in which the cyclohexadienone acetal group moves to an adjacent unit on the polymer chain. The oligomers with 2,6-dimethylphenol tail ends can be linked with the oligomers with substituted tail ends via this intramolecular rearrangement, in which quinol ether intermediates are present like in the oxidative coupling mechanism. Usually, the oxidative coupling is catalyzed with a CuCl/amine complex in the presence of oxygen. The amines, such as pyridine, N,N′-di-tert-butylethlenediamine (DBEDA), 4-(dimethylamino)pyridine (DMAP) and N,N,N′,N′-tetramethylthelenediamine (TMEDA), serve both as ligand for the copper ions and as bases to form phenolate anions, which are more easily oxidized. Besides the desired C–O coupling, C–C coupling of dimethylphenol can occur to form 3,3′,5,5′-tetramethylbicyclohexyldiene-2,2′,5,5′-tetrathene-4,4′-dione (3,3′,5,5′-tetramethyl-4,4′-diphenoxinolone, TMDPQ) which itself can serve as oxidant, leading to 3,3′,5,5′-tetramethyl-4,4′-biphenol (3,3′,5,5′-tetramethylbiphenyl-4,4′-diod). This bisphenol is subsequently incorporated into the polymer, yielding telechelics.15

Tail-end functionalized PPE can in principle be obtained by copolymerization.16–27 When using (besides the DMP) a para-functionalized phenol, which can only partake in the redistribution reactions, this phenol will always end up as the tail-end of PPE.28,29 However, rapid oxidative coupling will usually lead to large amounts of nonfunctionalized PPE as well. Furthermore, if one wants to use the commercially easily available ortho-unsubstituted phenols, extensive cross-linking9,30 and methyl group oxidation31,32 will occur.

Recently, we reported a method to perform redistribution reactions without oxidative coupling.33 This involves the use of copper catalysts either in the absence of oxygen, viz. CuCl/DMAP (ratio 1:1.6) under an inert argon atmosphere, or with ligands of low basicity, viz. Cu(NO3)2·3H2O/N-methylimidazole (NMI) (ratio 1:20) in air. These mild catalysts allow the tail-end introduction of various phenols, both ortho-substituted and ortho-unsubstituted, without oxidative side reactions. Since the added phenol was usually in excess with respect to the polymer, the redistribution results in a depolymerization. In contrast to the copolymerization technique, redistribution leads to PPE that is over 95% functionalized.

In this paper, we explore the scope and limitations of the clean redistribution reactions for the tail-end functionalization of PPE. A large range of mono- and difunctional phenols will be incorporated, and the formation of block copolymers between polystyrene and PPE will be demonstrated. Also, we will introduce TMDPQ as a much faster catalyst for the redistribution reactions. Although TMDPQ gives some side products, for practical applications its speed far outweighs these problems.

Results and Discussion

When PPE and a phenol are mixed together, the PPE is decreased in molecular weight in proportion to the degree of reaction with the phenol. Upon addition of 2,6-dimethylphenol (DMP) or the PPE dimer 4-(2,6-dimethylphenoxo)-2,6-dimethylphenol to a high molecular weight PPE, the latter is depolymerized yielding low molecular weight oligomers. The progress of the
polymer molecular weight decrease during the redistribution reaction using the PPE dimer is illustrated in the SEC analyses, presented in Figure 3. We used for this reaction a Cu(NO₃)₂·3H₂O/NMI catalyst, which hardly gives any polymerization due to the weakly basic ligands and the absence of additional base. A typical reaction time using this catalyst is 1–3 weeks using chloroform as solvent. In the PPE redistribution with DMP or PPE dimer the reaction product has the same structure as the starting polymer. Due to the addition of the phenol the polymer has a bimodal molecular weight distribution, but this becomes more monomodal during the equilibration reaction.

Figure 1. Oxidative coupling via quinol ether intermediates.

Figure 2. Redistribution (A) and intramolecular rearrangement (B) via ketal intermediates.

If the redistribution reaction is performed with a functional phenol, the reaction product has a different structure than the starting PPE. Whereas the starting polymer has a 2,6-dimethylphenoxy tail end, in the reaction product the functional phenol is incorporated as a tail end, for example 4-tert-butyl-2,6-dimethylphenol (2c). Due to the low oxidation potential of TBDMP, redistribution could be performed without the addition of any catalyst under air. When the reactions are performed under argon similar reaction rates are obtained. The ease of formation of phenoxy radicals in PPE is shown by a preliminary electron spin resonance (ESR) experiment. PPE dissolved in CDCl₃ already
shows the existence of 2,6-dimethylphenoxy endgroup radicals without the addition of an oxidant. In the ESR spectrum a septet signal with a hyperfine coupling of 5.6 G is observed, similar to that for the 2,6-dimethylphenoxy radicals described in the literature.34,35 Even though residual copper from the oxidative coupling might still be present in the PPE, no signals from copper are detected in the ESR spectrum. It is known that CHCl₃ and CDCl₃ can initiate radical chain reactions. This is an additional reason, beside its low oxidation potential, why for TBDMP redistribution no catalyst is needed.

During the redistribution with TBDMP, monofunctional PPE with a 2,6-dimethylphenoxy tail end is converted to a PPE with a tert-butyl substituent at its tail end. When the redistribution reaction is complete, all polymer chains contain a tert-butyl group at their tail end and almost no polymer chains are present with a 2,6-dimethylphenoxy tail end. This can be clearly seen from an HPLC analysis of the redistribution product, in which unfunctionalized PPE oligomers (total <5%) are detected as small peaks in between the large peaks from the oligomers with a tert-butyl tail end (Figure 4). The small peaks were identified as oligomers with a 2,6-dimethylphenoxy tail end or as telechelic PPE containing a tetramethylbiphenyl unit by the comparison with some model compounds, such as low molecular weight PPE oligomers. UV detection at 200 and 270 nm was used to differentiate between oligomers with a 2,6-dimethylphenoxy tail end (visible at 200 nm) and oligomers with incorporated tetramethylbiphenol (visible at 200 and 270 nm). Peaks A, B, and C, indicated in Figure 4, are typical peaks for oligomers with tert-

Figure 3. SEC analyses of redistribution PPE with PPE dimer, monitored in time.

Figure 4. HPLC analysis of PPE redistribution with 2c, obtained by evaporation of the solvent after 336 h reaction time, with UV detection at 200 and 270 nm. Peaks A, B, and C are typical peaks for oligomers with tert-butyl end groups, incorporated biphenyl units, and 2,6-dimethylphenyl end groups, respectively. Additional evidence for a complete redistribution was obtained from the ¹H-NMR spectrum (Figure 5) of the precipitated product, in which only the end groups of the modified PPE are present and no multiplet signal of the aromatic protons of the 2,6-dimethylphenoxy tail units of the starting PPE could be detected at a chemical shift of 7.09 ppm.

The observed complete redistribution, which leads to product consisting of predominantly tail-end modified PPEs and hardly any unmodified PPEs with a 2,6-dimethylphenoxy tail end, can be explained by the intermolecular rearrangement, which occurs next to the redistribution reaction (Figure 2). In the intermolecular rearrangement mechanism quinol ether intermediates are present, as in the oxidative coupling mechanism.

Attempted reactions of 4-tert-butyl-2,6-dimethylphenol (2c) with methoxy-terminated PPE did not result in a redistribution, which is consistent with the necessity of a phenolic endgroup in the quinone–ketal redistribution mechanism. Other experiments reported in literature also show the requirement of phenolic end groups on both of the reacting species.36–38 Recently, Baesjou39 and coworkers found that 4-(2,6-dimethylphenoxy)-2,6-dimethylanisole did not react in a redistribution in contrast to the PPE dimer with a free phenolic endgroup.
Redistribution Using CuCl/DMAP Catalysts.

When a CuCl/DMAP catalyst is employed in the PPE redistribution, oxidation of the methyl substituents can occur in the presence of oxygen. This oxidation, leading to ill-defined structures, can be suppressed by performing the reaction in the absence of oxygen, although redistribution rates are low. Under these mild conditions, ortho-unsubstituted phenols can also be incorporated as a tail end in PPE, without any cross-linking via the ortho-positions. This is in contrast to the oxidative coupling of phenol with only one ortho-substituent and an open para position, which usually yields highly branched and colored polymers.

A variety of end groups can be introduced by reacting different types of phenols in a PPE redistribution. Examples of ortho-unsubstituted phenols with a functional group at the para-position, which can be incorporated successfully as tail end using the CuCl/DMAP catalysts, are given in the Chart 1. The functional groups at the para-position are stable under the reaction conditions employed. As an example an 1H-NMR spectrum of a reaction product from a PPE redistribution with 4-phenylphenol (1f), using a CuCl/DMAP catalyst is shown in Figure 6. This spectrum shows no evidence for cross-linking via the ortho-positions. The proton at the ortho-position (indicated as proton 5) is shown by a doublet signal in the expected integral ratio in comparison with other protons from the endgroup (protons – [integral ratio]: 5/(3 + 4) – [1/2]; 5/2 – [1/1]; 5/1 – [2/1]; 5/6 – [1/1]).

Redistribution of 2c without the use of catalyst was already discussed before. Slightly improved reaction rates were found in a reaction under argon in the presence of a CuCl/DMAP catalyst. The conversion of 2c is also higher when a catalyst is employed. At a reaction time of 300 h the conversion of 2c without catalyst is 70%, while with the CuCl/DMAP catalyst the conversion of 2c is 90%. The allyl-terminated PPE, prepared by redistribution with 4-allyl-2,6-dimethylphenol (2b), is a precursor for various other functionalities. We converted the allyl-terminated PPE to a hydroxypropyl-terminated PPE by a hydroboration/oxidation reaction using bicyclo[3.3.1]nona-9-one (9-BBN) using a procedure described for allyl-terminated poly(methyl methacrylate).40

We tried to introduce a hydroxyalkyl substituent by redistribution with 4-hydroxymethyl-2,6-dimethylphenol, but reaction of this phenol predominantly yields a telechelic polymer with two PPE arms on a tetramethylbis(phenol)-formaldehyde core. Most probably this is due to the condensation reaction of two hydroxymethyl end groups. This is consistent with copolymerization experiments of 4-(hydroxymethyl)-2,6-dimethylphenol (2a) with 4-bromo-2,6-dimethylphenol as described by Percec.41 A more rational design for telechelic PPE would be the use of bis(phenols) during redistribution. For example, the telechelic product obtained above can also be obtained from a redistribution with bis(3,5-dimethyl-4-hydroxyphenyl)methane (tetramethylbis(phenol)-formaldehyde, 3c). This was tested with the CuCl/DMAP catalyst for bis(phenols) (3). The o-methyl-substituted bis(phenols) (3b and 3d) give higher reaction rates, analogous to the o-methyl-unsubstituted phenols (3a and 3c), and yielded the desired telechelics.
The PS anionic polymerization, as the reacting model compound 4-hydroxyphenyl-terminated polystyrene, prepared by copolymer synthesis. In this investigation, we employed DMAP catalysts in the absence of oxygen for the block copolymers. Redistribution reactions should be performed in more detail later.

This phenomenon will be illustrated in more detail later.

Redistribution experiments can also be used for the preparation of block copolymers. To obtain pure block copolymers, redistribution reactions should be performed using copper catalysts with low basic ligands or in the absence of oxygen. Therefore, we used CuCl/DMAP catalysts in the absence of oxygen for the block copolymer synthesis. In this investigation, we employed 4-hydroxyphenyl-terminated polystyrene, prepared by anionic polymerization, as the reacting model compound in the PPE redistribution (Figure 7). The PS–PPE diblock copolymers, which are prepared in this way, are characterized by size exclusion chromatography (SEC) with THF as eluent. The chromatograms are shown in Figure 8. SEC analyses of the starting polystyrene material implementing either a UV (254 nm) or RI detector overlap completely. Determined molecular weights are uncorrected and relative to a set of polystyrene standards. In case of the SEC analyses of the PS–PPE copolymers, the UV detector detects a higher apparent molecular weight than the RI detector. This is caused by the higher UV absorbance of PPE in comparison with PS. Block copolymers with a higher molecular weight contain a higher fraction of PPE and are more easily detected by UV than by RI detection. Furthermore, the determined SEC peaks are monomodal and symmetrical, which suggests that block copolymer formation has occurred. The determined molecular weights are summarized in Table 1. The employed phenol-terminated polystyrene is used as a model compound in the block copolymer synthesis via redistribution. The used polystyrene can be replaced by any phenol-terminated polymer, yielding numerous types of block copolymers, which will be demonstrated in the near future.

Redistribution Using Cu(NO₃)₂·3H₂O/N-Methylimidazole (NMI) Catalysts. Whereas reactions catalyzed by a CuCl/DMAP catalyst preferentially are performed in the absence of air, reactions using the Cu(NO₃)₂·3H₂O/NMI catalyst can be performed under air, which allows for a more convenient experimental setup. This catalyst is tested for redistributions with DMP and the PPE dimer as already presented before. Slightly higher redistribution rates are obtained when 2c is reacted in the presence of the Cu(NO₃)₂·3H₂O/NMI catalyst in comparison with an experiment in the absence of a catalyst. No large difference in reaction rates using the Cu(NO₃)₂·3H₂O/NMI catalyst or the CuCl/DMAP catalyst under argon is observed for redistribution with TBDMP. The bis(phenol) 4,4-bis(4-hydroxy-3,5-dimethylphenyl)pentanoic acid could also be incorporated successfully when reacted in chloroform and shows that redistribution is feasible in the presence of carboxylic acid functional groups without any side reactions. An advantage of the Cu(NO₃)₂·3H₂O/NMI catalyst in comparison to the CuCl/DMAP catalyst is that hardly any oxidation of the methyl substituents of the PPE occurs. Even when reactions are put under argon atmosphere, some minor oxidation still can occur when the CuCl/DMAP catalyst is used during long reaction times.

To prevent the formation of TMDPQ via C=C coupling of formed 2,6-dimethylphenol during redistribution, we used a high ligand–Copper ratio (L/Cu = 20). Lower L/Cu ratios can cause the formation of TMDPQ, which can be incorporated into PPE as well. This is in good agreement with the results previously reported in polymerization reactions. The CuCl/DMAP catalyst is used, a lower L/Cu ratio of 1.6 could be used; however, some minor TMDPQ formation still can occur.

Use of TMDPQ as Oxidant. Redistributions using copper catalysts did show clean redistributions; however, reaction rates are rather slow. To overcome this drawback TMDPQ is used as an oxidant. Reaction of TMDPQ with the phenolic endgroup of PPE will initially generate a phenoxyl radical endgroup and the diphenyl-1,1′-semiquinone. The semiquinone can couple with a polymer radical to form a quinone ketal (Figure 9) or abstract a hydrogen from a phenol to form 3,3′,5,5′-tetramethyl-4,4′-biphenol. Under the action of TMDPQ, hydrogen abstraction can presumably also occur from added functional phenols, and resulting phenoxy radicals can react in the redistribution reactions. TMDPQ can also lead to oxidative coupling, but only when a base is present; this will be illustrated later by an example.

Redistributions using TMDPQ are much faster, even in the absence of oxygen (reaction time 3–5 h), but yield less pure products because TMDPQ is also incorporated in the polymer. However, the speed far outweighs this disadvantage, especially for large scale applications.

<table>
<thead>
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<th>polymer type/detector</th>
<th>Mₙ</th>
<th>Mₘ</th>
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<tr>
<td>PS</td>
<td>2.97 × 10³</td>
<td>3.28 × 10³</td>
<td>1.11</td>
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<tr>
<td>RI detector</td>
<td>3.00 × 10³</td>
<td>3.29 × 10³</td>
<td>1.10</td>
</tr>
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<td>5.99 × 10³</td>
<td>12.40 × 10³</td>
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<tr>
<td>UV detector</td>
<td>4.66 × 10³</td>
<td>10.80 × 10³</td>
<td>2.32</td>
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</table>
Also the PPE that is used for the redistribution is of different quality in these applications. While in the redistribution experiments with copper catalysts, as described before, well-defined PPEs prepared by precipitation polymerization are used, redistributions using TMDPQ as oxidant are performed using commercially available PPE grades. Already 80–100% of the polymer chains in these commercially available PPE grades contain a tetramethylbiphenyl unit derived from TMDPQ. The aromatic C–H protons of the tetramethylbiphenyl unit coming from TMDPQ are visible at 7.36 ppm in the $^1$H-NMR spectrum. Besides this tetramethylbiphenyl unit, commercially available PPE also contains Mannich base type end groups. In particular, signals belonging to Mannich base end groups derived from di-n-butylamine are visible in the $^1$H-NMR spectrum. Assignments of the proton signals from these di-n-butylamine Mannich base type end groups are described by Mitui.48,49

The incorporation of TMDPQ also means that the catalyst is consumed and that the redistribution will not reach completion. Therefore, increased phenol incorporation is observed, when the TMDPQ is added gradually instead of an addition of all TMDPQ at the beginning of the reaction. Due to incomplete redistribution, the reaction product contains, besides the modified PPEs with the reacted phenol incorporated as a tail end, also unfunctionalized polymers, either with a 2,6-dimethylphenoxy tail or telechelic PPE with incorporated tetramethylbiphenyl. The aromatic C–H protons of the 2,6-dimethylphenoxy tail units are visible as a multiplet signal at 7.09 ppm in the $^1$H-NMR spectrum. o-Methyl-substituted phenols typically can yield PPE chains of which 80 mol % contains functionalized end groups, 15 mol % contains a tetramethylbiphenyl unit, and 5 mol % has a 2,6-dimethylphenoxy tail end as determined by $^1$H-NMR spectroscopy. An optimized reaction of PPE with ortho-unsubstituted phenols using TMDPQ as oxidant typically yields 35 mol % unfunctionalized PPE containing a tetramethylbiphenyl unit, 5 mol % unfunctionalized PPE with 2,6-dimethylphenoxy tail ends, and 60 mol % modified PPE. The lower percentage is due to the fact that the formed 3,3′,5,5′-tetramethyl-4,4′-biphenol derived from TMDPQ is more easily incorporated than the phenols without a methyl group at the ortho-positions. Despite the fact that not all PPE molecules are functionalized, these PPEs are still very useful in applications like reactive extrusion.

PPE redistribution with phenols, including some functional ones, was described in detail by White.50 The use of TMDPQ in redistribution reactions has extensively been studied by General Electric Plastics,51–54 for phenols also containing functional groups like carboxylic acid functionalities.55 The use of commercially available ortho-unsubstituted phenols (4) is investigated in a PPE redistribution using TMDPQ as oxidant.

Some of these functional phenols barely dissolve in toluene, which is the best commercially applicable solvent for PPE. Therefore, we predissolve these functional phenols in methanol and perform the reactions in a mixture of toluene and methanol (5–10 vol %). The solubility in toluene or toluene/methanol mixtures can be improved further by attaching a facilely removable protective group onto the functional groups. The solu-
bility of tyramine (4-(aminoethyl)phenol) can be enhanced by a tert-butoxy carbonyl (t-BOC) protective group. The t-BOC-group is readily removable using trifluoroacetic acid or by heat, for instance during polymer extrusion. The solubility of carboxylic acids is increased by transforming them to their methyl esters. Elevated reaction temperatures (approximately 60 °C) are used to improve solubility of phenols and PPE. Since electron transfer reactions play an important role in the redistribution, only a small influence of temperature on reaction rate is observed.

Besides the improvement of the solubility of the reacting phenol, the intrinsic reactivity of the phenol is influenced by the type of substituent. Usually, phenols with electron-donating substituents react more rapidly in a redistribution due to their lower oxidation potential.\textsuperscript{33} O-Methyl-substituted functional phenols are not commercially available, so we investigated functional tetramethylbis(phenols) (5), which easily can be synthesized via an acid-catalyzed condensation of 2,6-dimethylphenol and functional ketones, e.g. 4-oxopentanoic acid. Functional bis(phenols) (5) tested in a PPE redistribution employing TMDPQ as oxidant are listed in Chart 1.

As reported above for redistributions with bis(phenol) acetone (BPA) or bis(phenol) formaldehyde (BPF) and their o-methyl-substituted derivatives, ortho-unsubstituted bis(phenols) react only at one side of the bis(phenol) while o-methyl-substituted bis(phenols) react at both sides of the bis(phenol). Also for the bis(phenol) derived from 4-oxopentanoic acid the same phenomenon occurs, as is illustrated in a \textsuperscript{1}H-NMR spectrum of a product from redistribution with an ortho-unsubstituted bis(phenol), 4,4-bis(4-hydroxyphenyl)pentanoic acid methyl ester (5b) (Figure 10A). The \textsuperscript{1}H-NMR spectrum of this bis(phenol), which is incorporated at the tail end, typically shows four doublet signals of the aromatic protons. Furthermore, the \textsuperscript{1}H-NMR spectrum shows a singlet belonging to the aromatic C–H protons of the 2,6-dimethylphenoxo unit adjacent to the bis(phenol) tail unit at 6.77 ppm. A similar singlet was observed for the aromatic protons in the penultimate benzene ring in PPEs modified with ortho-unsubstituted phenols (1 and 4) at their tail end. Redistribution with o-methyl-substituted bis(phenols) yields telechelics with two PPE arms. This is illustrated by the \textsuperscript{1}H-NMR spectrum (Figure 10B) of a redistribution product from 4,4-bis(4-hydroxy-3,5-dimethylphenyl)pentanoic acid methyl ester (5d).

The Role of Base. The necessity of a base for the oxidative polymerization\textsuperscript{10,36–62} is confirmed by reactions of TMDPQ with 2,6-dimethylphenol (DMP) in the presence or absence of a base. If TMDPQ is brought into reaction with DMP in equimolar amounts, almost no oligomers are formed as determined by size exclusion chromatography (SEC) (Figure 11). Only the bipherol and TMDPQ are present in the reaction product and no C–O coupling occurs. The \textsuperscript{1}H-NMR spectrum (Figure 12) of the reaction mixture of DMP and TMDPQ shows that no C–O coupling occurs but only C–C coupling occurs because signals of the 2,6-dimethylphenoxy repeating units at 6.5 ppm are absent. The C–C coupling leads to formation of 3,3′,5,5′-tetramethyl-4,4′-bis(phenol). This is consistent with the necessity of a high amine/copper ratio to prevent C–C coupling during the copper-catalyzed oxidative polymerization of DMP.\textsuperscript{43–46}

![Figure 10](image-url)
matic C–H of the penultimate unit is shifted slightly upfield in comparison to one in a redistribution with an ortho-unsubstituted phenol. Presumably, when a base is absent a dimethyl-substituted ketal (Figure 1, $R_1 = H$ and $R_2 = CH_3$) is formed more easily than a monomethyl substituted quinol ether (Figure 2, $R_1 = R_3 = H$ and $R_2 = CH_3$).

When additional base, like a pyridine/DMAP combination, is added, incorporation also occurs in the middle of the chain, and considerably higher molecular weights are obtained. The aromatic C–H protons of a 2,6-dimethylphenoxy units, adjacent to a cresol unit show a singlet at 6.67 ppm in the 1H-NMR spectrum as depicted in Figure 13B. This signal has a larger integral in comparison with a signal from two aromatic C–H protons of a cresol tail unit. Consequently, more aromatic C–H protons of a 2,6-dimethylphenoxy units adjacent to a cresol unit are present. Besides o-cresol tail units, additional signals are present at 7.09 ppm in the 1H-NMR spectrum (Figure 13B), presumably coming from 2,6-dimethylphenoxy tail units. Most probably the reaction product consists of a mixture with different polymer structures, i.e., either with 2,6-dimethylphenoxy or cresol tail units and either with or without one or more cresol units in the middle of the polymer chain.

**Conclusions**

A facile method is described for the preparation of functional PPE oligomers or telechelics. Redistribution of PPE with a phenolic compound yields a product with that phenolic compound incorporated as tail end. A large variety of end groups, including reactive end groups, can be introduced in this way. Phenolic compounds which dissolve in a good solvent for PPE and are not too deactivated by steric hindrance or electron-withdrawing substituents are suitable for the described redistribution reaction. Furthermore, block copolymers can be prepared by reacting a phenol-terminated polymer in a redistribution with PPE.
Depending on the reacting phenolic compound, desired reaction time and product purity, TMDPQ or copper/amine systems can be used as a catalyst. For a fast PPE redistribution with ortho-unsubstituted phenols, without any oxidation of methyl substituents of the PPE chain, we prefer the use of TMDPQ. For the preparation of pure oligomers and block copolymers, we prefer a slow redistribution using copper catalysts in the absence of oxygen, especially when o-methyl-substituted phenols are employed.

**Experimental Section**

**Materials.** DMP, TMDPQ and internal grades of PPE, PPE-1 (IV = 0.40 dl/g, tolue, 30 °C), and PPE-2 (IV = 0.46 dl/g, tolue, 30 °C), were supplied by General Electric Plastics, Bergen op Zoom, The Netherlands. The DMP was recrystallized from n-hexane before use. Low molecular weight PPEs were obtained using a precipitation polymerization method.61 CuCl (99% pure, 4-dimethylaminopyridine (DMAP) 99% pure, 4-oxopentanoic acid (98% pure), benzoyl peroxide (97% pure), and tert-butyl hydroperoxide (99% pure) were obtained from Fluka. Tetramethylbis(phenol) endgroup, 7.09 (2H, s, aromatic C head endgroup), 6.36 (2H, s, aromatic C – H head endgroup), M	extsubscript{n} = 1.19 × 10	extsuperscript{4}.

Redistribution of 2c with PPE. PPE (10 g, M	extsubscript{n} = 3.5 × 10	extsuperscript{5}, 83.17 mmol of dimethylphenol repeating units, prepared by precipitation polymerization62) was dissolved in toluene (100 mL). Upon the addition of 2c (4.55 g, 25.5 mmol), the PPE is depolymerized to low molecular weight oligomers. After a reaction time of 13 days, the reaction mixture was precipitated into methanol. 

Redistribution with 4-(2,6-Dimethylphenoxy)-2,6-dimethylphenol (PPE Dimer) using a Cu(NO	extsubscript{3})	extsubscript{2}-3H	extsubscript{2}O/NMI catalyst. A mixture of Cu(NO	extsubscript{3})	extsubscript{2}-3H	extsubscript{2}O (0.053 g, 0.22 mmol) and N-methylimidazolide (0.355 g, 4.3 mmol) was added to a solution of PPE – OH (1.07 g, M	extsubscript{n} = 7.3 × 10	extsuperscript{3}) and DMP (0.617 g, 5.0 mmol) in chloroform (10 mL). The reaction was performed in the presence of air at room temperature. Reaction samples were taken and extracted subsequently with an aqueous 10 wt % EDTA solution and aqueous 37% HCl, and then the product was obtained by evaporation of the chloroform.

Redistribution with 4-(2,6-Dimethylphenoxymethyl)phenol (PPE Dimer) using a Cu(NO	extsubscript{3})	extsubscript{2}-3H	extsubscript{2}O/NMI catalyst. A mixture of Cu(NO	extsubscript{3})	extsubscript{2}-3H	extsubscript{2}O (0.025 g, 0.10 mmol) and N-methylimidazolide (0.175 g, 2.1 mmol) was added to a solution of PPE – OH (0.233 g, M	extsubscript{n} = 7.3 × 10	extsuperscript{3}) and DMP (0.200 g, 0.83 mmol) in chloroform (10 mL). The reaction was performed in the presence of air at room temperature. Reaction samples were taken and extracted subsequently with an aqueous 10 wt % EDTA solution and aqueous 37 % HCl, and then the product was obtained by evaporation of the chloroform.

Redistribution with 5c Using a Cu(NO	extsubscript{3})	extsubscript{2}-3H	extsubscript{2}O/NMI Catalyst. PPE – OH (1.57 g, M	extsubscript{n} = 7.3 × 10	extsuperscript{3}) and 5c (0.595 g, 1.74 mmol) were dissolved in chloroform (10 mL) at 60 °C. When all PPE and most of the added bis(phenol) were dissolved, the reaction mixture was allowed to cool to room temperature. Then a mixture of Cu(NO	extsubscript{3})	extsubscript{2}-3H	extsubscript{2}O (0.098 g, 0.40 mmol) and N-methylimidazolide (0.663 g, 8.1 mmol) in chloroform (10 mL) was added. The reaction was performed in the presence of air at room temperature. Reaction samples were taken and extracted subsequently with an aqueous 10 wt % EDTA solution and aqueous 37% HCl, and then the product was obtained by evaporation of the chloroform.

Redistribution with 1f Using a CuCl/DMAP Catalyst. PPE-1 (2.54 g). If (0.82 g, 4.31 mmol). CuCl (0.010 g, 0.10 mmol) and DMAP (0.020 g, 0.16 mmol) were set under argon by repeated evacuation of the flask and filling with argon. The reaction was started by the addition of 30 mL of chloroform. After 17 days the reaction mixture was extracted with a 10 wt % EDTA solution and a 10 wt % HCl solution and precipitated into methanol (300 mL). The precipitated polymer was collected by filtration and dried in a vacuum oven at 60 °C. The number average molecular weight of the precipitated polymer is determined by single-beam NMR spectroscopy: M	extsubscript{n} = 2.33 × 10	extsuperscript{3}. 

**Techniques.** 

**H-NMR** spectra were obtained using a 400 MHz Bruker AM-400 spectrometer using CDCl	extsubscript{3} or CD	extsubscript{3}OD as solvent. All δ values are given in ppm downfield from tetramethylsilane at 0 ppm. Functionality contents are calculated using a	extsubscript{C}=2.3,5,6-hexachloro-p-xylene were obtained from Aldrich. The PPE dimer, 4-(2,6-dimethylphenoxymethyl)-2,6-dimethylphenol, was obtained from P. J. Baeijou from the Leiden Institute of Chemistry, Leiden University, Leiden, The Netherlands. The TBDMS-protected 4-hydroxyphenyl-terminated polystyrene was prepared by M. Hempenius, Twente University of Technology, The Netherlands, using a literature procedure.42

**Synthesis of Bis(3,5-dimethyl-4-hydroxyphenyl)pentanoic Acid (5c).** DMP (597.0 g, 4.89 mol) and 4-oxopentanoic acid (levulinic acid) (283.7 g, 2.44 mol) were dissolved at 60 °C, and a solution of 715 mL of 37% HCl was slowly added. Subsequently 7 g (36.8 mmol) of p-toluenesulfonic acid monohydrate was added. The reaction mixture was reacted for 5 days at 60 °C, and then 3 L water was added. The product was filtrated and washed with 0.5 L water. The filtrated product was recrystallized twice from toluene and dried in a vacuum oven. Reaction yield: 80% δ-NMR (400 MHz, CD	extsubscript{3}OD): δ 1.46 (3H, s, CH	extsubscript{3}), 2.14 (12H, s, CH	extsubscript{3}), 2.31 (2H, t, J = 8.1 Hz, CH	extsubscript{2}OH, t, 1H, CH	extsubscript{2}OH), 6.72 (4H, s, Ar–H), 4.69 (2H, s, Ar–OH). 

**GPC** apparatus, PL gel columns 103 and 105 Å, and a Waters Equipment used for this analysis are a Waters 150-CV ALC/DEP system equipped with a Waters 410 differential refractometer and a Waters 486 tunable absorbance detector (UV detection at 254 nm). The number average molecular weight of the meniscus was measured using a Stuart Scientific Melting point apparatus SMP2 using a heating rate of 2 °C/min.
biphenyl tail end group), 7.10 (2H, d, J = 8.6 Hz, aromatic C5–H biphenyl tail end group), 6.81 (2H, s, C6–H aromatic penultimate 2,6-dimethylphenoxy unit at tail end), 6.34 (2H, s, aromatic C8–H 2,6-dimethylphenolic head unit).

**PPE Redistribution with 4e Using TMDPQ.** PPE-1 (30.14 g) was dissolved in toluene (300 mL) at 60 °C. Subsequently, 4e (1.811 g, 13.1 mmol) dissolved in methanol (15 mL) was added. The reaction was started by the addition of TMDPQ (0.033 g, 0.14 mol). After 4 h of reaction time, the reaction mixture was precipitated in methanol (3.5 L). The precipitated polymer was collected by filtration and dried in a vacuum oven at 90 °C. The obtained polymer was reprecipitated from a 10 wt% chloroform solution in a 10-fold excess of methanol. Yield of precipitated product: 28.0 g. 1H-NMR (400 MHz, CDCl3): δ 3.88 (2H, t, J = 6.4 Hz, HOCH3). 2.87 (2H, t, J = 6.5 Hz, CH2–Ar), 7.21 (2H, d, J = 8.4 Hz, ortho C3–H aromatic tail end group), 7.00 (2H, d, J = 8.6 Hz, meta C4–H aromatic tail end group), 6.71 (2H, s, C–H aromatic penultimate unit at tail end), 6.37 (2H, s, aromatic C3–H head unit). Functionality (phenol) content in precipitated polymer: 1.85 wt %.

Uncorrected molecular weights determined by SEC, eluent CHCl3 using poly styrene standard specimen: \( M_n = 6.59 \times 10^3 \) and \( M_w = 15.55 \times 10^3 \).

**PPE Redistribution with 5b Using TMDPQ.** PPE-1 (3.94 g, 13.1 mmol) dissolved in methanol (10 mL) was added. The reaction was started by the addition of TMDPQ (0.3024 g, 1.26 mmol). After 4 h of reaction time, the reaction mixture was precipitated in methanol (3.5 L). The precipitated polymer was collected by filtration and dried in a vacuum oven at 90 °C. The obtained polymer was reprecipitated from a 10 wt% chloroform solution in a 10-fold excess of methanol. Yield of precipitated product: 9.60 g. 1H-NMR (400 MHz, CDCl3): δ 7.00 × 103 Hz, aromatic H aromatic penultimate 2,6-dimethylphenoxy unit at tail end), 6.66 (2H, s, aromatic C–H penultimate tail end group), 7.15 (2H, t, J = 2.7 Hz, aromatic para C–H tail end group), 6.93 (2H, d, J = 8.1 Hz, aromatic ortho C–H tail end group), 7.17 (2H, m, aromatic meta C–H’s tail end group).

Uncorrected molecular weights determined by SEC, eluent CHCl3 using poly styrene standard specimen: \( M_n = 7.00 \times 10^3 \) and \( M_w = 17.65 \times 10^3 \).

**PPE Redistribution with 5d Using TMDPQ.** PPE-1 (10.00 g) was dissolved in toluene (100 mL) at 60 °C. Subsequently, 5d (0.7722 g, 2.17 mmol) dissolved in methanol (10 mL) was added. The reaction was started by the addition of TMDPQ (0.033 g, 0.14 mol). After 1 and 2 h of reaction time again TMDPQ was added (2 × 0.033 g, 0.14 mol). After 5 h of total reaction time, the reaction mixture was precipitated in methanol (1.5 L). The precipitated polymer was collected by filtration and dried in a vacuum oven at 90 °C. The obtained polymer was reprecipitated from a 10 wt% chloroform solution in a 10-fold excess of methanol. Yield of precipitated product: 29.4 g. 1H-NMR (400 MHz, CDCl3): δ 3.62 (3H, s, OCH3), 7.15 (2H, d, J = 8.8 Hz, aromatic C2–H tail end group), 7.08 (2H, d, J = 8.7 Hz, aromatic C3–H tail end group), 6.74 (2H, d, J = 8.6 Hz, aromatic C1–H tail end group), 6.76 (2H, s, C5–H aromatic penultimate unit at tail end), 6.37 (2H, s, aromatic C3–H head unit).

Functionality (phenol) content in precipitated polymer: 3.56 wt %.

Uncorrected molecular weights determined by SEC, eluent CHCl3 using poly styrene standard specimen: \( M_n = 7.00 \times 10^3 \) and \( M_w = 17.65 \times 10^3 \).

**PPE Redistribution with 5d Using TMDPQ.** PPE-1 (1.19 g, 11.0 mmol), dissolved in methanol (15 mL), 7a (1.15 g, 10.6 mmol), dissolved in methanol (5 mL), and DMP (0.4745 g, 3.88 mol) and DMAP (0.0570 g, 0.467 mmol) were dissolved in pyridine (5 mL) and reacted for 5 h at 60 °C. After 4 h of reaction time, the reaction mixture was precipitated into methanol. The obtained product was collected by filtration and dried in a vacuum oven at 90 °C. The reaction proceeded in the presence of base.

**Redistribution of 7a with PPE Under the Action of TMDPQ.** PPE-2 (4.98 g, 41.4 mol dimethylphenylxylene repeating units) was dissolved in toluene (30 mL) at 60 °C. Then, 7a (1.15 g, 10.6 mmol), dissolved in methanol (5 mL), was added, and the reaction was started upon addition of TMDPQ (0.0502 g, 0.21 mmol). After a reaction time of 4 h, the reaction mixture was precipitated into methanol. The product was reprecipitated twice from chloroform into methanol. 1H-NMR (CDCl3): δ 6.66 (2H, s, aromatic C–H penultimate tail end group), 7.15 (2H, t, J = 2.7 Hz, aromatic para C–H tail end group), 6.93 (2H, d, J = 8.1 Hz, aromatic ortho C–H tail end group), 7.17 (2H, m, aromatic meta C–H’s tail end group).

Uncorrected molecular weights determined by SEC, eluent = CHCl3 using poly styrene standard specimen: \( M_n = 5.07 \times 10^3 \) and \( M_w = 20.20 \times 10^3 \).

**Redistribution of 7a with PPE Under the Action of TMDPQ and Base.** PPE-2 (5.00 g, 41.6 mmol dimethylphenylxylene repeating units) and DMAP (0.531 g, 4.35 mmol) were dissolved in toluene (25 mL) and pyridine (25 mL) at 60 °C. Then 7a (1.19 g, 11.0 mmol), dissolved in methanol (5 mL), was added, and the reaction was started by the addition of TMDPQ (0.0504 g, 0.21 mmol). After a reaction time of 4 h, the reaction mixture was precipitated into methanol. The product was reprecipitated twice from chloroform into methanol. Uncorrected molecular weights determined by SEC, eluent = CHCl3 using poly styrene standard specimen: \( M_n = 14.50 \times 10^3 \) and \( M_w = 42.00 \times 10^3 \).

**Reaction of DMP with TMDPQ.** In the Absence of Base. TMDPQ (0.8307 g, 3.46 mol) and DMP (0.4765 g, 3.90 mol) were dissolved in toluene (5 mL) and reacted for 5 h at 60 °C. The reaction was stopped by evaporation of the solvent. The reaction product consisted of a mixture of TMDPQ and 3,7,5,5′-tetramethyl-4,4′-biphenol in a molar ratio of 4:1, as determined by 1H-NMR spectroscopy. 1H-NMR (CDCl3) TMDPQ: 7.2 (4H, s, aromatic C–H), 2.16 (12H, s, CH3). 1H-NMR (CDCl3) 4,4′-bis(3,5-dimethylphenyl): 7.15 (4H, s, aromatic C–H), 4.59 (12H, s, CH3) (5.00 g).

In the Presence of Base. TMDPQ (0.8290 g, 3.45 mol), DMP (0.4745 g, 3.88 mol) and DMAP (0.0570 g, 0.467 mmol) were dissolved in pyridine (5 mL) and reacted for 5 h at 60 °C. The reaction was stopped by evaporation of the solvent. Then the reaction mixture was dissolved into chloroform and extracted with 10 wt% HCl solution, to remove pyridine and DMAP. Subsequently, the chloroform was evaporated off.
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References and Notes

(33) Baesjou, P. J.; Challa, G.; Reedijk, J. personal communication.