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

Huub A. M. van Aert, Marcel H. P. van Genderen, Grègory J. M. L. van Steenpaal, Laurent Nelissen, and E. W. Meijer*

Eindhoven University of Technology, PO Box 513, 5600 MB Eindhoven, The Netherlands

Juraj Liska

General Electric Plastics, PO Box 117, Bergen op Zoom, The Netherlands

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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 reacting 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 mechanism[6−11] 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*-butylethylenediamine (DBEDA), 4-(dimethylamino)pyridine (DMAP) and *N*,*N*,*N*′,*N*′-tetramethylethylenediamine (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′-tetramethylbicyclohexylidene-2,2′,5,5′-tetraene-4,4′-dione (3,3′,5,5′-tetramethyl-4,4′-diphenoquinone, TMDPQ) which itself can serve as oxidant, leading to 3,3′,5,5′-tetramethyl-4,4′-biphenol (3,3′,5,5′-tetramethylbiphenyl-4,4′-diol). This bis(phenol) 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-linking[9,30] and methyl group oxidation[31,32] 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. $Cu(NO_3)_2 \cdot 3H_2O$/*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-dimethylphenoxy)-2,6-dimethylphenol to a high molecular weight PPE, the latter is depolymerized yielding low molecular weight oligomers. The progress of the

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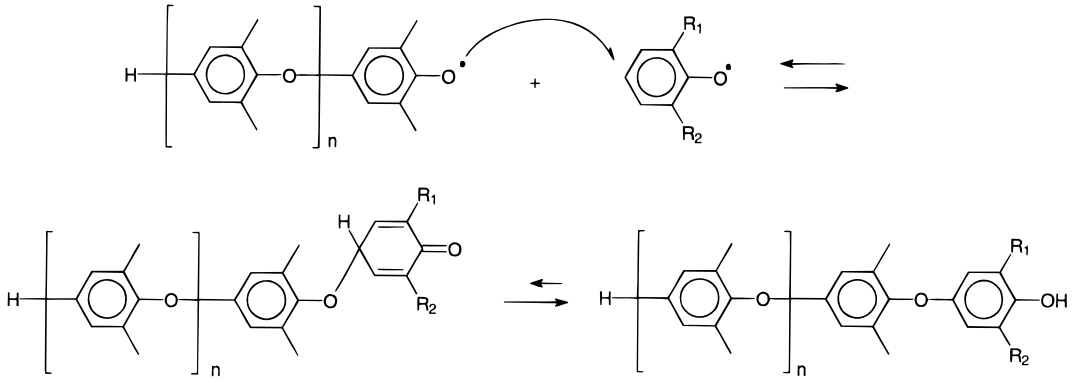


Figure 1. Oxidative coupling via quinol ether intermediates.

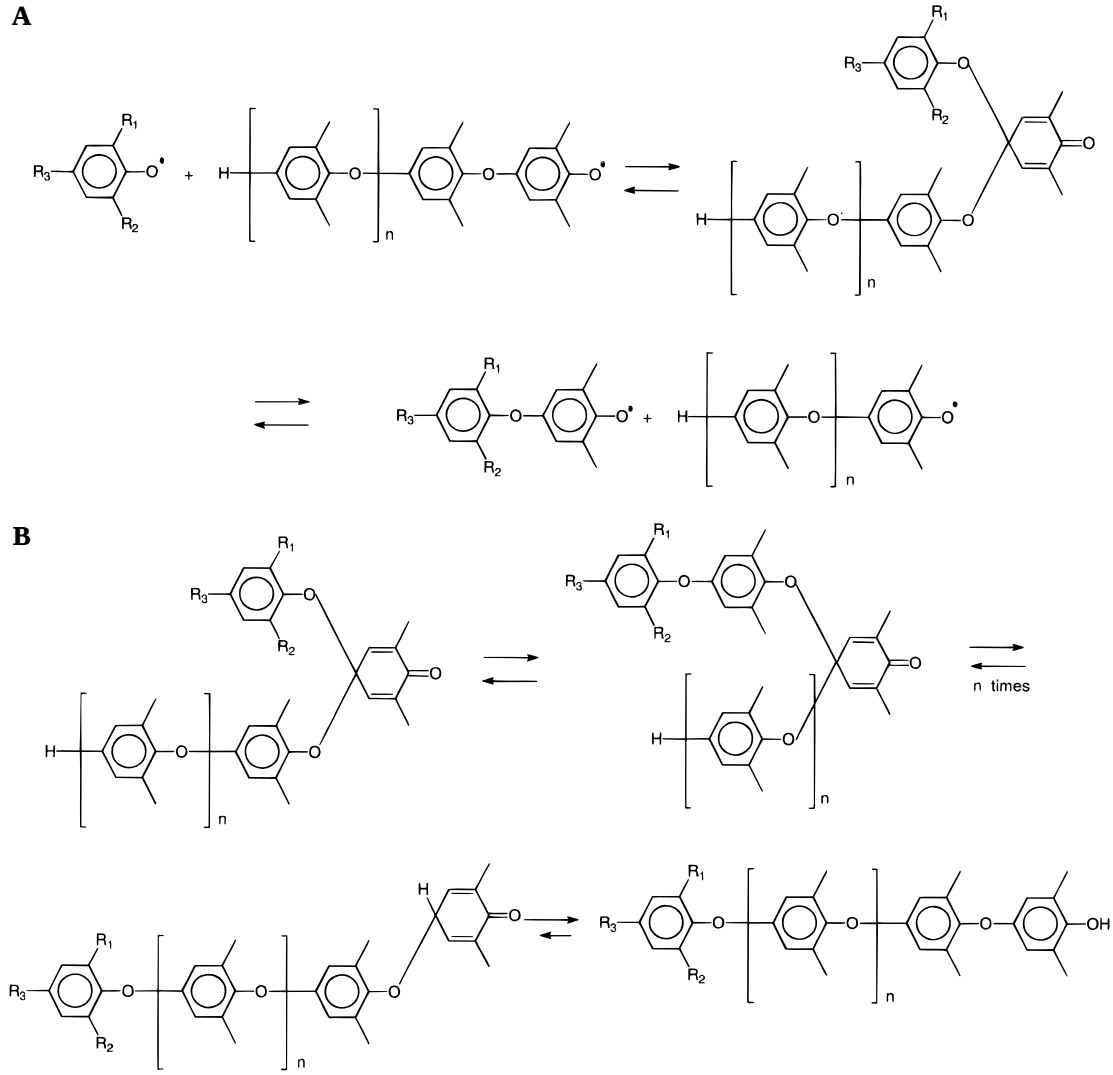


Figure 2. Redistribution (A) and intramolecular rearrangement (B) via ketal intermediates.

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 $Cu(NO_3)_2 \cdot 3H_2O$/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.

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 $CDCl_3$ already

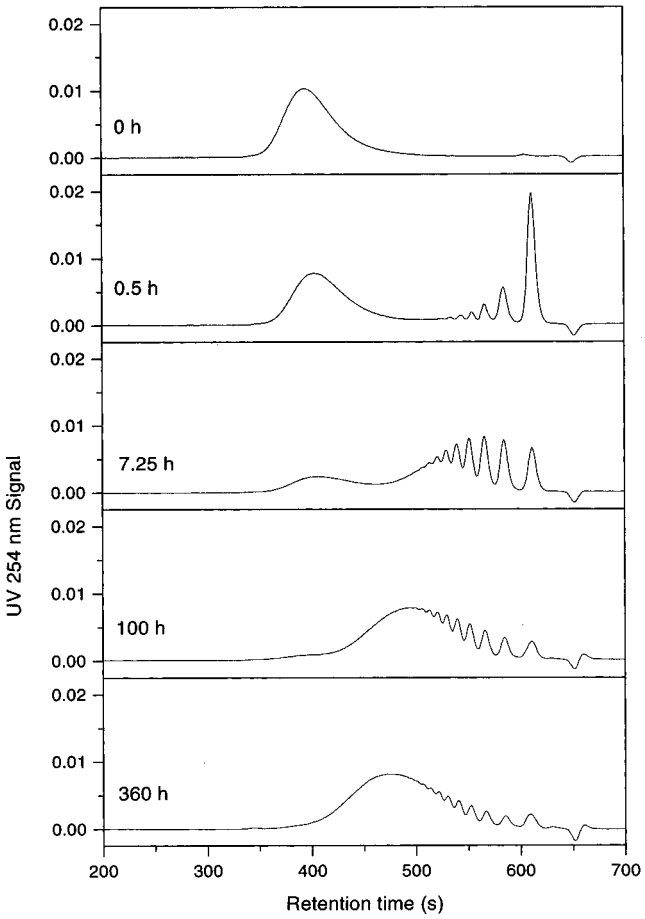


Figure 3. SEC analyses of redistribution PPE with PPE dimer, monitored in time.

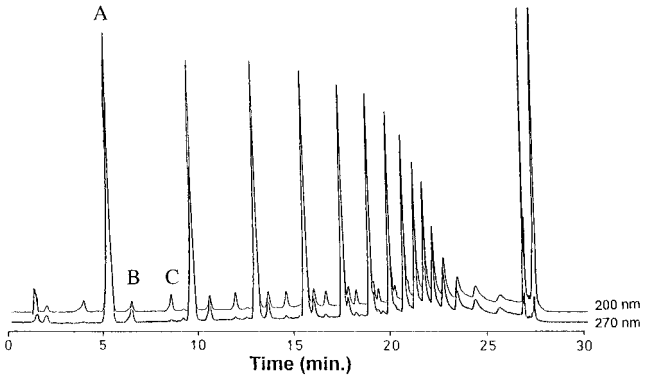


Figure 4. HPLC analysis of PPE redistribution with **2c**, obtained by evaporation of the solvent after 336 h reaction time, with UV detection at 200 and 270 nm. Peaks A, B, and C are typical peaks for oligomers with tert-butyl end groups, incorporated biphenyl units and 2,6-dimethylphenyl end groups, respectively.

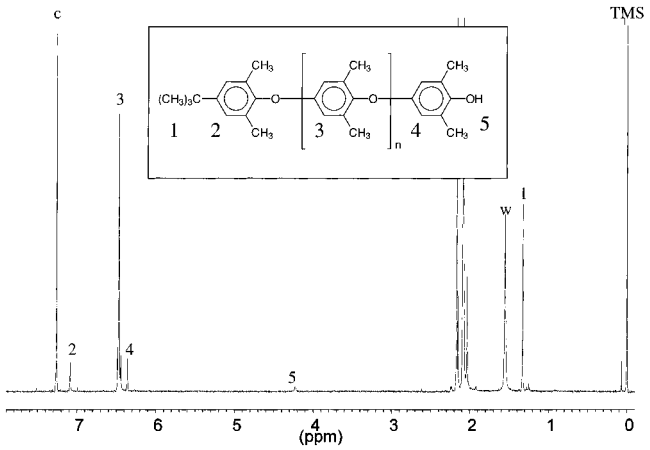


Figure 5. ^{1}H-NMR spectrum ($CDCl_3$, 400 MHz) of the precipitated product from a PPE redistribution with **2c** after 336 h reaction time. The signals marked with w and c are assigned to residual H_2O and $CHCl_3$, respectively.

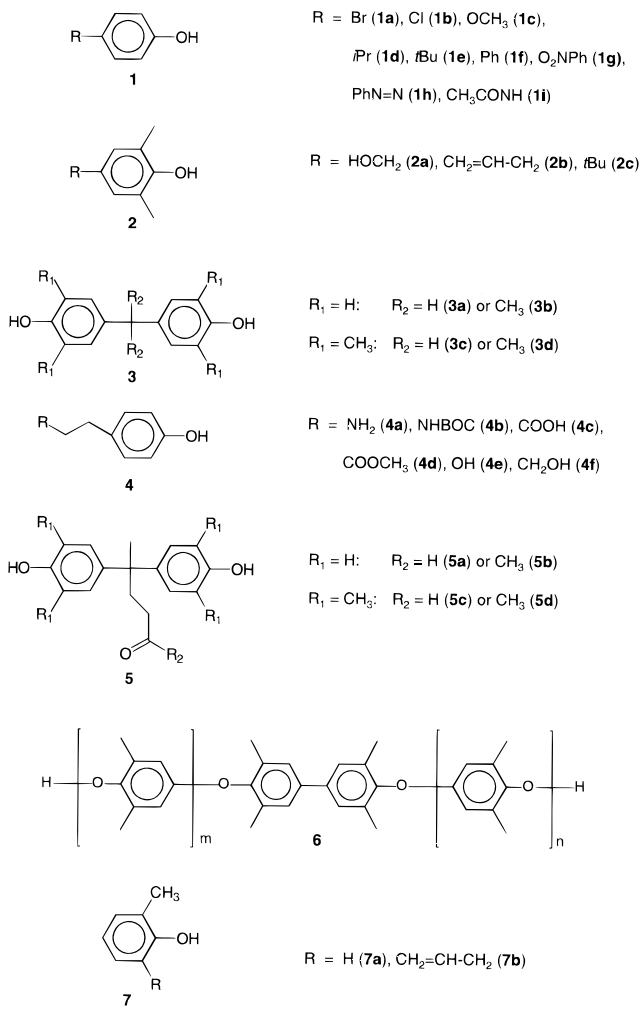
shows the existence of 2,6-dimethylphenoxy endgroup radicals without the addition of an oxidant. In the ESR spectrum a septet signal with a hyperfine coupling of 5.6 G is observed, similar to that for the 2,6-dimethylphenoxy radicals described in the literature.[34,35] Even though residual copper from the oxidative coupling might still be present in the PPE, no signals from copper are detected in the ESR spectrum. It is known that $CHCl_3$ and $CDCl_3$ 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 sustituent 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 tetramethylbiphenol 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*-butyl end groups, incorporated biphenyl units, and 2,6-dimethylphenyl end groups, respectively. Additional evidence for a complete redistribution was obtained from the ^{1}H-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, Baesjou[39] 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.

Chart 1



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 (**1**), 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 a ^{1}H-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]).

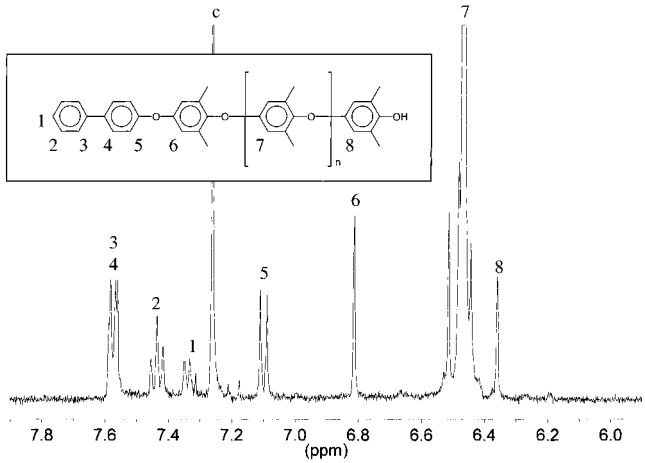


Figure 6. ^{1}H-NMR spectrum (aromatic region) of the reprecipitated reaction product from PPE redistribution with **1f**; the signal marked with c is assigned to residual $CHCl_3$.

Usually, phenols with electron-donating substituents react more rapidly in a redistribution due to their lower oxidation potential. A phenol with an electron-withdrawing substituent, like 4-nitrophenol, barely shows any reactivity. If we introduce a phenyl group as spacer, like in 4-nitrophenylphenol (**1g**), or if a phenol like 3-nitrophenol with the nitro-substituent in the *meta*-position is used, then a higher reactivity is found.

o-Methyl-substituted phenols (**2**) are intrinsically more reactive due to the electron-donating methyl groups. The ones we employed in a PPE redistribution using the CuCl/DMAP catalyst are listed in Chart 1. Typical reaction times employed for the *o*-methyl-substituted phenols are 1−2 weeks, whereas *ortho*-ususbstituted phenols are reacted usually for 3−4 weeks. 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]nonan-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. E.g. 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.

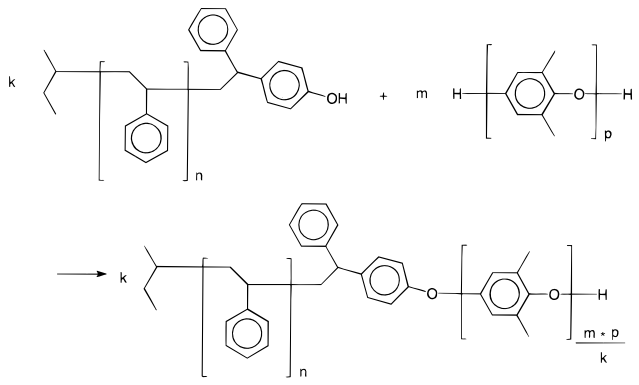


Figure 7. PPE redistribution with phenol-terminated PS

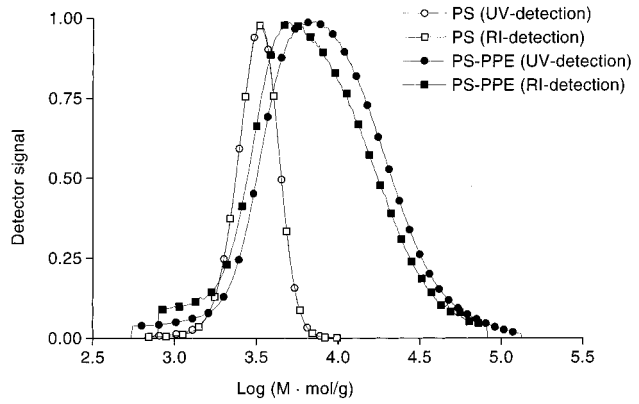


Figure 8. SEC chromatograms of phenol-terminated PS and prepared PS−PPE diblock copolymers.

When using *ortho*-unsubstituted bis(phenols) (**3a**, **3b**, **5a**, and **5b**) in the PPE redistribution, reaction occurs surprisingly only at one side of the bis(phenol) yielding a different type of telechelic, presumably due to a higher oxidation potential. 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).[42] 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 demonstrated in the near future.

Table 1. Uncorrected Molecular Weights As Determined by SEC

polymer type/detector	$\bar{M}_n$	$\bar{M}_w$	D
PS			
UV detector	2.97×10^3	3.28×10^3	1.11
RI detector	3.00×10^3	3.29×10^3	1.10
PS−PPE			
UV detector	5.99×10^3	12.40×10^3	2.07
RI detector	4.66×10^3	10.80×10^3	2.32

Redistribution Using $Cu(NO_3)_2 \cdot 3H_2O$/*N*-Methylimidazole (NMI) Catalysts. Whereas reactions catalyzed by a CuCl/DMAP catalyst preferentially are performed in the absence of air, reactions using the $Cu(NO_3)_2 \cdot 3H_2O$/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 $Cu(NO_3)_2 \cdot 3H_2O$/NMI catalyst in comparison with an experiment in the absence of a catalyst. No large difference in reaction rates using the $Cu(NO_3)_2 \cdot 3H_2O$/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 (**5c**) 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 $Cu(NO_3)_2 \cdot 3H_2O$/NMI catalyst in comparison to the CuCl/DMAP catalyst is that hardly any oxidation of the methyl substitutents 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.[43−46] If 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 phenoxy radical endgroup and the diphenosemiquinone. 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.[47]

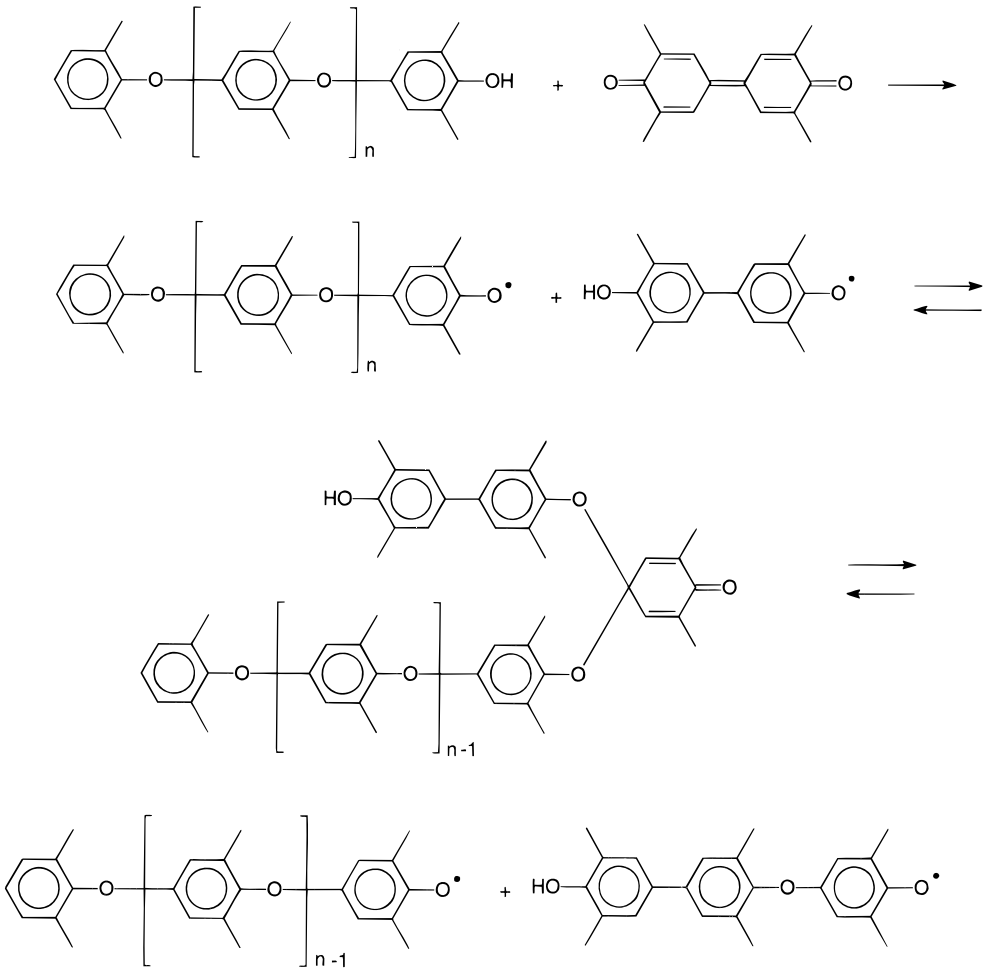


Figure 9. Reaction of TMDPQ with PPE.

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*-postitions. 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 by 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.[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 ^{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 ^{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 ^{1}H-NMR spectrum shows a singlet belonging to the aromatic C−H protons of the 2,6-dimethylphenoxy 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 ^{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[18,56−60] 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 biphenol and TMDPQ are present in the reaction product and no C−O coupling occurs. The ^{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.[43−46]

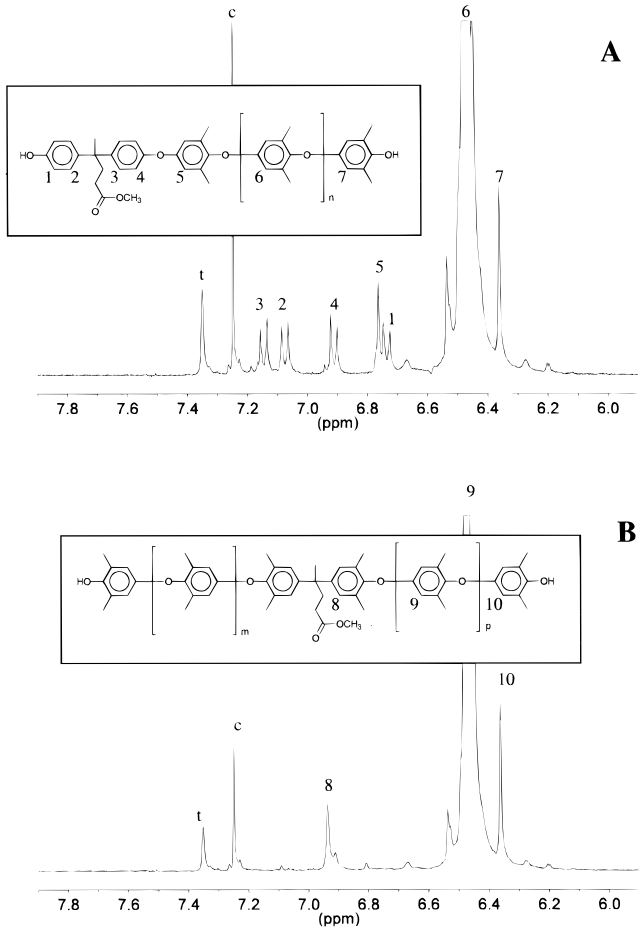


Figure 10. (A) ^{1}H-NMR spectrum of a reprecipitated product from PPE redistribution with **5b**. (B) ^{1}H-NMR spectrum of reprecipitated product from a PPE redistribution with **5d**. The signals marked with t and c are assigned to incorporated TMDPQ and $CHCl_3$, respectively.

However, when base is present, e.g. a combination of DMAP and pyridine, higher molecular weight oligomers are formed. All these oligomers contain the biphenyl unit coming from TMDPQ (**6**). When a base is present, the rate of oxidative coupling can be increased since DMP generates more easily the phenolate anion, from which the phenoxy radical is formed. This is consistent with the necessity of a base to produce a phenolate as an intermediate in the copper-catalyzed oxidative polymerization. The slower reaction of DMP with TMDPQ in comparison with the reaction of TMDPQ with a polymeric phenol endgroup can be explained by the higher redox potential of the monomeric species.[29]

The importance of an additional base for the occurrence of oxidative coupling besides the redistribution with TMDPQ as oxidant is illustrated by experiments with *para*-unsubstituted phenols, like *o*-cresol derivatives (**7**).

When redistributions are performed with *para*-unsubstituted phenols, like *o*-cresol (**7a**), in the absence of a base the reacting phenol is only incorporated at the polymer tail end. This can be seen clearly from the ^{1}H-NMR spectrum of a redistribution product with **7a**, as shown in Figure 13A. The cresol unit at the tail end of the polymer shows as expected one triplet of the *para* C−H proton, one doublet of the *ortho* C−H proton and two overlapping signals of the *meta* C−H protons in the aromatic region. Furthermore a singlet is shown for the penultimate 2,6-dimethylphenoxy unit. All peaks have the expected integral ratios. The singlet for the aro-

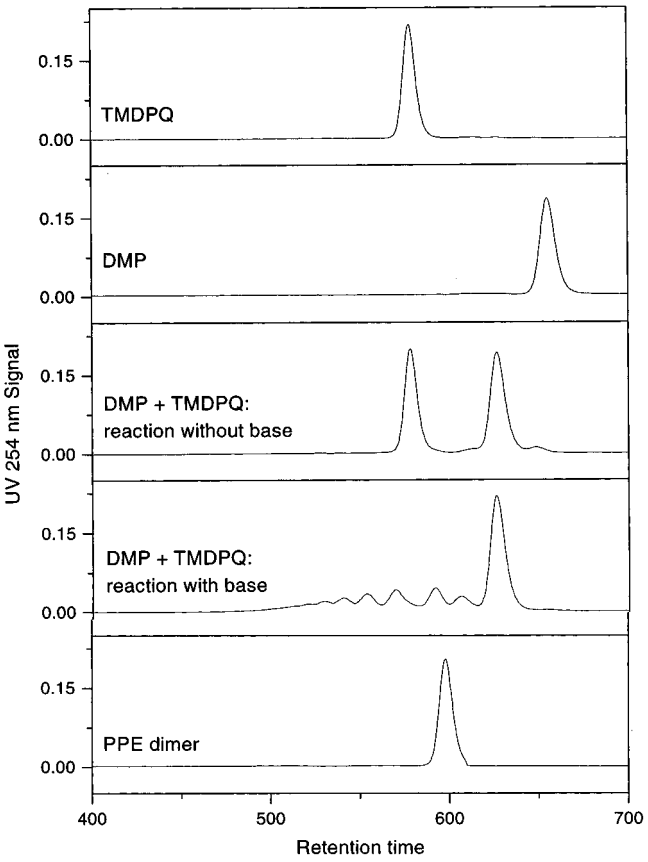


Figure 11. SEC of reaction products of DMP and TMDPQ, in the presence or absence of pyridine/DMAP, including SEC of references like DMP, TMDPQ, and 4-(2,6-dimethylphenoxy)-2,6-dimethylphenol (PPE dimer). The reactions of DMP with TMDPQ yield product mixtures containing 3,3′,5,5′-tetramethylbiphenyl-4,4′-diol.

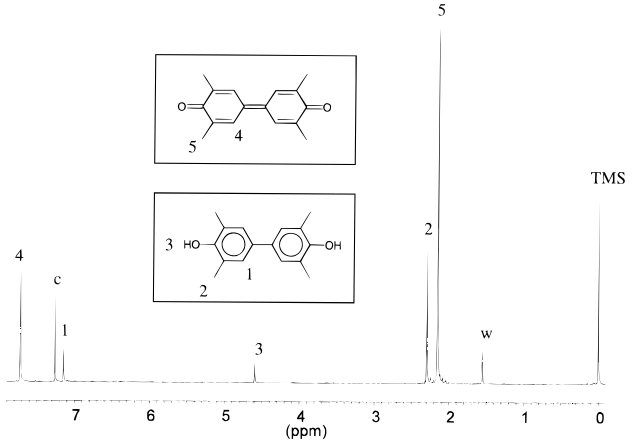


Figure 12. ^{1}H-NMR spectrum in $CDCl_3$ of the reaction product from reaction of DMP and TMDPQ in the absence of a base. The signals marked with w and c are assigned to residual H_2O and $CHCl_3$, respectively.

matic C−H of the penultimate unit is shifted slightly upfield in comparison to one in a redistribution with a *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 then 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-

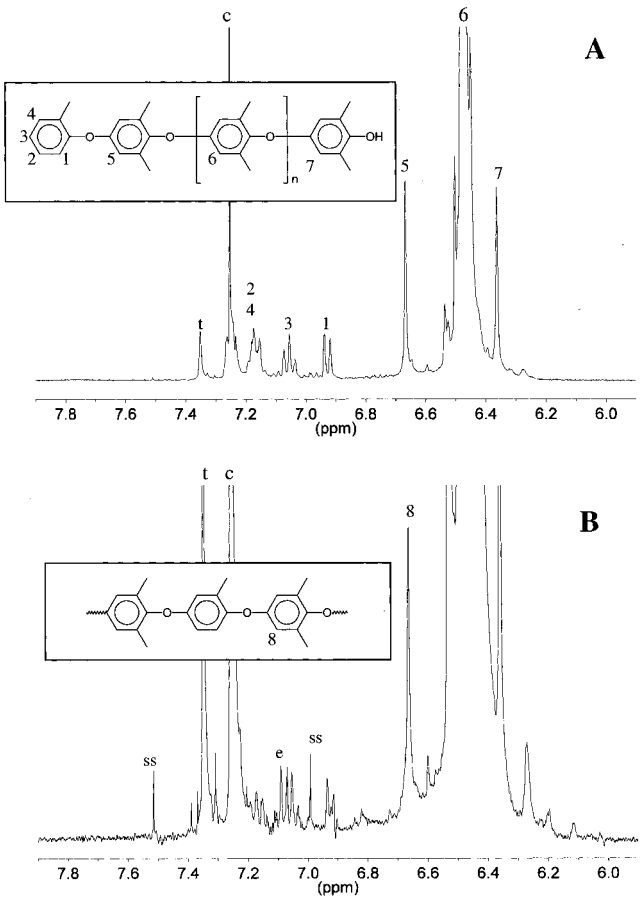


Figure 13. ^{1}H-NMR spectrum of precipitated reaction product of redistribution with **7a**: (A) without addition of pyridine/DMAP; (B) with addition of pyridine/DMAP. The signals marked with t, c, ss, and e are assigned to incorporated TMDPQ, residual $CHCl_3$, spinning side bands, and 2,6-dimethylphenoxy tail units, respectively.

dimethylphenoxy units, adjacent to a cresol unit show a singlet at 6.67 ppm in the ^{1}H-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 ^{1}H-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, toluene, 30 °C), and PPE-2 (IV = 0.46 dL/g, toluene, 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, *N*-methylimidazole 99%, *p*-toluenesulfonic acid monohydrate 99% pure and a 1 M solution of tetrabutylammonium fluoride (TBAF) in THF were obtained from Acros. 4,4-Bis(4-hydroxyphenyl)pentanoic acid (**5a**) >98% pure and 4-phenylphenol (**1f**) >95% pure were obtained from Fluka. Tetramethylbis(phenol)−acetone (**3d**)[62] and 4-*tert*-butyl-2,6-dimethylphenol (**2c**)[63] were prepared according to literature procedures. The solvents chloroform, hexane, pyridine, THF, methanol and toluene, and copper(II) nitrate trihydrate were used p.a. from Merck. Ethylenediaminetetraacetic acid trisodiumsalt hydrate (EDTA) 95% pure, *ortho*-cresol 99+% pure, benzoyl peroxide 97% and α,α′-2,3,5,6-hexachloro-*p*-xylene were obtained from Aldrich. The PPE dimer, 4-(2,6-dimethylphenoxy)-2,6-dimethylphenol, was obtained from P. J. Baesjou 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]

Techniques. ^{1}H-NMR spectra were obtained using a 400 MHz Bruker AM-400 spectrometer using $CDCl_3$ or CD_3OD as solvent. All δ values were given in ppm downfield from tetramethylsilane at 0 ppm. Functionality contents are calculated using α,α′-2,3,5,6-hexachloro-*p*-xylene as an internal standard (400 MHz $CDCl_3$: 2H, $\delta = 4.93$ ppm). HPLC analysis is performed using a HP 1090 HPLC with a reversed phase column, type 10007C18, and a diode array detector. A gradient from a 30% acetonitrile/water mixture to 100% acetonitrile at 40 °C was employed over 20 min. The presented size exclusion chromatography (SEC) analysis in Figure 3 was performed at room temperature using chloroform as eluent, an LC-10AT Shimadzu liquid chromatograph with a PL gel column (particle size, 5 μm; pore size, 500 Å; length, 300 mm; internal diameter, 7.5 mm) and UV detection at 254 nm using a Linear UVIS-205 absorbance detector. Molecular weight determination of all other PPEs was performed using SEC at General Electric Plastics using a chloroform/ethanol mixture (98/2 v/v) as eluent at 40 °C. Dibutylamine (50 ppm) is added to prevent tailing. Equipment used for this analysis are a Waters 150-CV ALC/GPC apparatus, PL gel columns 10^3 and 10^5 Å, and a Waters 490E programmable multiwavelength detector (PPE detected at 280 nm, polystyrene standards detected at 254 nm). The PS−PPE block copolymers are analysed by SEC with THF as eluent at 40 °C using a Waters model 510 SEC apparatus, 2 Shodex KF 80-M linear columns, a Waters 410 differential refractometer and a Waters 486 tunable absorbance detector (UV detection at 254 nm). Element analysis has been performed using a Perkin Elmer CHN analyzer type 2400. Melting points were measured using a Stuart Scientific melting point apparatus SMP2 using a heating rate of 2 °C/min.

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% ^{1}H-NMR (400 MHz, CD_3OD): δ 1.46 (3H, s, CH_3), 2.14 (12H, s, CH_3), 2.31 (2H, t, J = 8.1 Hz, CH_2−COOH), 2.05 (2H, t, J = 8.1 Hz, CH_2−CH_2−COOH), 6.72 (4H, s, Ar−*H*), 4.69 (2H, s, Ar−O*H*). ^{13}C-NMR (400 MHz, CD_3OD): δ 176.6 ($CH_3C(Ar)_2CH_2CH_2$*C*OOH), 152.0 (aromatic C1), 141.6 (aromatic C4), 128.3 (aromatic C3), 124.9 (aromatic C2), 45.1 (CH_3*C*$(Ar)_2CH_2CH_2COOH$), 37.8 ($CH_3C(Ar)_2$*C*H_2CH_2COOH), 31.1 ($CH_3C(Ar)_2CH_2$*C*H_2COOH), 28.2 (*C*$H_3C(Ar)_2CH_2CH_2COOH$), 16.9 (Ar−*C*H_3). Mp 202 °C. Anal. Calcd for $C_{21}H_{22}O_4$: C, 73.66; H, 7.65; Found: C, 73.46; H, 7.62.

The experimental procedures described in this Experimental Section for redistribution experiments are typical examples and are also valid for other phenols

Redistribution of 2c with PPE. PPE (10 g, $\bar{M}_n = 3.5 \times 10^3$, 83.17 mmol of dimethylphenoxy repeating units, prepared by precipitation polymerization[61]) 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. ^{1}H-NMR ($CDCl_3$): δ 1.33 (9H, s, $C(CH_3)_3$ tail endgroup), 7.09 (2H, s, aromatic C−H tail endgroup), 6.36 (2H, s, aromatic C−H head endgroup), $\bar{M}_n = 1.19 \times 10^3$.

PPE Redistribution with DMP Using a $Cu(NO_3)_2$·$3H_2O$/NMI Catalyst. A mixture of $Cu(NO_3)_2$·$3H_2O$ (0.053 g, 0.22 mmol) and *N*-methylimidazole (0.355 g, 4.3 mmol) was added to a solution of PPE−OH (1.07 g, $\bar{M}_n = 7.3 \times 10^3$) 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.

PPE Redistribution with 4-(2,6-Dimethylphenoxy)-2,6-dimethylphenol (PPE Dimer) using a $Cu(NO_3)_2$·$3H_2O$/NMI catalyst. A mixture of $Cu(NO_3)_2$·$3H_2O$ (0.025 g, 0.10 mmol) and *N*-methylimidazole (0.175 g, 2.1 mmol) was added to a solution of PPE−OH (0.233 g, $\bar{M}_n = 7.3 \times 10^3$) and the PPE dimer (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.

PPE Redistribution with 5c Using a $Cu(NO_3)_2$·$3H_2O$/NMI Catalyst. PPE−OH (1.57 g, $\bar{M}_n = 7.3 \times 10^3$) 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 $Cu(NO_3)_2$·$3H_2O$ (0.098 g, 0.40 mmol) and *N*-methylimidazole (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.

PPE Redistribution with 1f Using a CuCl/DMAP Catalyst. PPE-1 (2.54 g), **1f** (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 90 °C. The number average molecular weight of the precipitated polymer is determined using ^{1}H-NMR spectroscopy: $\bar{M}_n = 2.33 \times 10^3$. ^{1}H-NMR (400 MHz, $CDCl_3$): δ 7.57 (4H, m, aromatic *ortho* C3−H and aromatic *meta* C4−H biphenyl tail end group), 7.43 (2H, t, J = 7.6 Hz, aromatic *meta* C2−H biphenyl tail end group), 7.34 (1H, m, aromatic C1−H

biphenyl tail endgroup), 7.10 (2H, d, $J = 8.6$ Hz, aromatic *ortho* C5−H biphenyl tail endgroup), 6.81 (2H, s, C6−H aromatic penultimate 2,6-dimethylphenoxy unit at tail end), 6.36 (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 (0.3024 g, 1.26 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 precipitated product: 28.0 g. ^{1}H-NMR (400 MHz, $CDCl_3$): δ 3.88 (2H, t, $J = 6.4$ Hz, HOCH_2), 2.87 (2H, t, $J = 6.5$ Hz, CH_2−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), 6.77 (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 $CHCl_3$, using polystyrene standard specimen: $\bar{M}_n = 6.59 \times 10^3$ and $\bar{M}_w = 15.55 \times 10^3$.

PPE Redistribution with 5b Using TMDPQ. PPE-1 (30.01 g) was dissolved in toluene (300 mL) at 60 °C. Subsequently, **5b** (3.94 g, 13.1 mmol) dissolved in methanol (30 mL) was added. The reaction was started by the addition of TMDPQ (0.300 g, 1.25 mol). After 3 h reaction time, the reaction mixture was precipitated in methanol (4 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. ^{1}H-NMR (400 MHz, $CDCl_3$): δ 3.62 (3H, s, OCH_3), 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), 6.91 (2H, d, $J = 8.7$ Hz, C4−H aromatic 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 $CHCl_3$, using polystyrene standard specimen: $\bar{M}_n = 7.00 \times 10^3$ and $\bar{M}_w = 17.65 \times 10^3$.

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 precipitated product: 9.60 g. ^{1}H-NMR (400 MHz, $CDCl_3$): δ 3.65 (3H, s, OCH_3), 6.93 (4H, s, aromatic C−H bis(phenol) core unit), 6.36 (2H, s, C3−H aromatic head unit). Functionality (phenol) content in precipitated polymer: 5.79 wt %. Uncorrected molecular weights determined by SEC, eluent = $CHCl_3$, using polystyrene standard specimen: $\bar{M}_n = 5.80 \times 10^3$ and $\bar{M}_w = 16.00 \times 10^3$.

PPE Redistribution with 5c Using Benzoyl Peroxide. PPE-1 (10.01 g) was set under argon by repeated evacuation of the flask and filling with argon. Toluene (100 mL), distilled from sodium, was added to the PPE powder and PPE was dissolved at 90 °C. Subsequently, **5c** (0.250 g, 0.73 mmol) dissolved in methanol (5 mL) was added. The reaction was started by the addition of benzoyl peroxide (0.100 g, 0.41 mol). After 3 h of reaction time, the reaction mixture was precipitated in methanol (1.2 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: 9.62 g. ^{1}H-NMR (400 MHz, $CDCl_3$): δ 6.94 (4H, s, aromatic C−H bis(phenol) core unit), 6.36 (2H, s, C3−H aromatic head unit). Functionality (phenol) content in precipitated polymer: 1.76 wt %. Uncorrected molecular weights determined by SEC, eluent = $CHCl_3$, using polystyrene standard specimen: $\bar{M}_n = 9.50 \times 10^3$ and $\bar{M}_w = 24.50 \times 10^3$.

Preparation of PS−PPE Diblock Copolymers via Redistribution. The anionically prepared polystyrene (PS), initiated by *sec*-butyllithium, was terminated by a 1,1-divinylethene derivative containing a *tert*-butyldimethylsilyl (TBDMS) protected phenol, 1-(4-(*tert*-butyldimethylsiloxy)phenyl)-1-phenylethylene, according to a literature procedure.[42] Deprotection of the TBDMS group was performed using tetrabutylammonium fluoride (TBAF) in THF according to the following procedure: 0.594 g of PS terminated with a TBDMS protected phenolic endgroup ($\bar{M}_n = 3.0 \times 10^3$) was dissolved in 15 mL of THF, and 1 mL of a 1 M solution of TBAF in THF was added. After 4 days of reaction at room temperature, the reaction mixture was extracted twice with an aqueous 15 wt % HCl solution and precipitated into methanol. The obtained product was collected by filtration and dried in a vacuum oven at 60 °C. SEC (THF): $\bar{M}_n = 3.0 \times 10^3$, $\bar{M}_w = 3.3 \times 10^3$, $D = 1.1$.

Redistribution of the phenol-terminated PS and PPE was performed according to the following experimental procedure: 0.222 g of phenol-terminated PS ($\bar{M}_n = 3.0 \times 10^3$), 0.230 g of PPE-1, 0.031 g of DMAP, and 0.016 g of CuCl were set under argon by repeated evacuation of the flask and filling with argon. The reaction was started by the addition of chloroform (15 mL). After reaction during 1 week at room temperature, the reaction mixture was precipitated into methanol. The obtained product was collected by filtration and dried in a vacuum oven at 60 °C.

Redistribution of 7a with PPE Under the Action of TMDPQ. PPE-2 (4.98 g, 41.4 mol of 2,6-dimethylphenoxy repeating units) was dissolved in toluene (50 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 the 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. ^{1}H-NMR ($CDCl_3$): δ 6.66 (2H, s, aromatic C−H penultimate tail endgroup), 7.15 (1H, t, $J = 2.7$ Hz, aromatic *para* C−H tail endgroup), 6.93 (1H, d, $J = 8.1$ Hz, aromatic *ortho* C−H tail endgroup), 7.17 (2H, m, aromatic *meta* C−H's tail endgroup). Uncorrected molecular weights determined by SEC, eluent = $CHCl_3$, using polystyrene standard specimen: $\bar{M}_n = 5.07 \times 10^3$ and $\bar{M}_w = 20.20 \times 10^3$.

Redistribution of 7a with PPE Under the Action of TMDPQ and Base. PPE-2 (5.00 g, 41.6 mmol dimethylphenoxy repeating units) and DMAP (0.531 g, 4,35 mmol) are 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 = $CHCl_3$, using polystyrene standard specimen: $\bar{M}_n = 14.50 \times 10^3$ and $\bar{M}_w = 42.00 \times 10^3$.

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 3,3′,5,5′-tetramethyl-4,4′-biphenol in a molar ratio of 4/1, as determined by ^{1}H-NMR spectroscopy. ^{1}H-NMR ($CDCl_3$) TMDPQ: 7.72 (4H, s, aromatic C−H), 2.16 (12H, s, CH_3). ^{1}H-NMR ($CDCl_3$) 4,4′-bis(3,5-dimethyl)biphenyl: 7.15 (4H, s, aromatic C−H), 4.59 (1H, s, OH), 2.30 (12H, s, CH_3).

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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