The Course of the Copper-Catalyzed Oxidative Polymerization of 2,6-Dimethylphenol. Analysis of Oligomeric Phenols during the Coupling Reaction

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ABSTRACT: The course of the copper-catalyzed oxidative coupling of 2,6-dimethylphenol (DMP) has been studied by HPLC-analysis of reaction mixtures which had started with either DMP itself, or with its C−O coupled dimer, 4-(2′,6′-dimethylphenoxy)-2,6-dimethylphenol, under both aerobic and anaerobic conditions. These measurements have provided information on how the actual phenol coupling step takes place and how the polymerization reaction proceeds. In reactions started with the monomer, no or at most very small amounts of oligomers of DMP are detected, apart from a precipitate of polymeric material in the aerobic experiments. Reactions started with the dimer only result in swift formation of significant amounts of monomer in addition to oligomers. This difference in behavior can be ascribed to the higher reactivity of oligomeric phenols compared to the monomer. The fact that monomer phenol is formed from dimer phenol is strong evidence for a reaction pathway in which a quinone ketal is formed by C−O coupling of two phenolic moieties. It is believed that as long as this quinone remains coordinated to the copper, it can decompose by (probably heterolytic) fission of one of the ether bonds to generate two (new) species, de facto resulting in *redistribution* of the oligomers. Once the quinone dissociates from the copper catalyst, a *rearrangement* may occur to afford the C−O coupled phenol. Methylated phenols (anisoles) do not take part in either redistribution or rearrangement reactions, since a quinone ketal can only be formed from species that can be deprotonated, i.e., from phenols.

Introduction

The homogeneous, copper/amine-catalyzed, oxidative coupling of 2,6-dimethylphenol (DMP), as shown schematically in Figure 1, has been extensively investigated after its discovery in 1959 by A. S. Hay.[1] During this coupling reaction a polymer, poly(phenylene ether) (PPE), is formed by (repeated) C−O coupling of phenolic moieties. This polymer possesses excellent mechanical properties and chemical stability, even at elevated temperatures, and is therefore an important engineering plastic.[2,3] The other product of this reaction is formed by C−C coupling of two monomeric phenols, resulting in an intensely colored, undesired side-product, viz. diphenoquinone (DPQ[4]), which degrades the polymer upon further processing at high temperatures. No other products are known to be formed in significant amounts.[5]

The research performed on this reaction has been mainly occupied with the reaction mechanism in terms of the role of the copper catalyst in the initial steps of the oxidative coupling of DMP, especially with respect to the nature of copper species involved in this reaction.[6] Early mechanistic proposals involve mononuclear copper−phenoxo complexes as intermediates generating phenoxyl radicals as the active species.[2,7,8] However, recent proposals are more inclined toward a mechanism featuring dinuclear copper−phenoxo species, which produce phenoxonium cations as active species.[9−17]

However, the questions of how the actual phenol coupling takes place after the initial phenol oxidation and how the polymerization reaction proceeds also need to be addressed. Several groups have studied this topic already in some detail,[2,9,10,12,18−21] and a variety of proposals have been made, ranging from electrophilic and nucleophilic (both ionic) to radical coupling mechanisms. In a previous publication,[22] the results of theoretical calculations of atomic charges of monomeric and dimeric species of DMP have been discussed, to obtain an understanding of the most likely coupling pathway. From this study it was concluded that the most likely pathway is one that involves the formation of a quinone ketal intermediate. Several experimental findings also supported this possibility.[23−29] The most conclusive results have been obtained by Cooper and Mijs,[23,26] when a reaction was started with pure 4-(2′,6′-dimethylphenoxy)-2,6-dimethylphenol (the dimer of DMP); after only a short period monomer DMP had been formed by a redistribution reaction, i.e. "decomposition" of the quinone ketal. However, only qualitative results were obtained with these experiments, as in some cases thin-layer chromatography was used for analysis[26] and in other cases the oligomeric phenols in a reaction mixture were converted into silyl ethers[23−25] (with

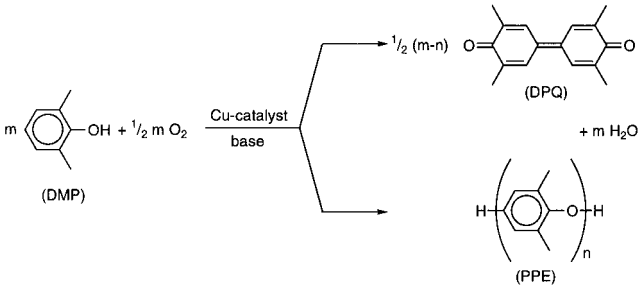

Figure 1. Overall reaction scheme for the oxidative coupling of DMP to PPE and DPQ.

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possible loss of product) which were subsequently analyzed by gas chromatography. Therefore, it was deemed necessary that some of these measurements had to be studied in more detail, to obtain more quantitative results. HPLC was chosen as the method for analyzing the oligomers of DMP in reaction mixtures of reactions started with either the monomer or the dimer.

Experimental Section

General Data. Solvents (methanol, *n*-hexane) were obtained from Baker as analytical grades. Acetonitrile was of HPLC quality from Rathburn. Water was of Millipore quality. $Cu(NO_3)_2 \cdot 3H_2O$, K_2CO_3, and iodine were of analytical grades from Merck and were used without further treatment. 2,6-Dimethylphenol (reagent grade) was purchased from Baker and was purified by repeated crystallization from *n*-hexane prior to use. *N*-Methylimidazole (Nmiz; 99% pure) was used as obtained from Janssen. Sodium methoxide (95%) was obtained from Aldrich, and was found to have an active base content of 97%. The amounts of sodium methoxide used were corrected for this content. Crystals of $Cu(Nmiz)_4(NO_3)_2$ were prepared as described earlier,[15] and were powdered prior to use. 4-(2′,6′-Dimethylphenoxy)-2,6-dimethylanisole and 4-(2′,6′-dimethylphenoxy)-2,6-dimethylphenol (dimer) were synthesized as described before.[17] 4-*tert*-Butyl-2,6-dimethylphenol (TBDMP) was received as a gift from H. van Aert (Eindhoven University of Technology). Hydrochloric acid solutions were derived from a 0.100 M stock solution in water, prepared from a Titrisol package obtained from Merck.

^{1}H NMR spectra were recorded on a JEOL JNM-FX (200 MHz) FT-NMR spectrometer in $CDCl_3$ solvent, with TMS as an internal reference.

HPLC analysis was performed with a system consisting of a Separations GT-103 in-line degassing unit, a Gynkotek high-precision pump model 480, a Rheodyne 7125 injection valve, an Alltech column prefilter, a Spherisorb S5 ODS2 C18 reversed phase column, and an Applied Biosystems 759A absorbance detector. Measurements were carried out by using gradient elution with eluents A and B, these being a mixture of water/acetonitrile (7/3 v/v) and pure acetonitrile, respectively. The elution program was as follows: 2.5 min A, followed by a linear increase of B content to 100% at $t = 22.5$ min, and finally pure B until $t = 40$ min. DMP and its oligomers were detected by UV absorbance at 195 nm.

Experiments with Monomer and Dimer. The catalyst solution used in all experiments consisted of a 4 mM $Cu(NO_3)_2$ solution with 30 equiv of Nmiz in methanol (Nmiz/Cu = 30). The substrate solution was prepared by mixing, in a 25 mL volumetric flask, 5 mL of a 0.04 M solution of the phenol (monomer or dimer) in methanol and 1 mL of a 0.1 M of a methanolic solution of NaOMe and filling the flask up to 25 mL with methanol, resulting in a 8 mM phenol and 4 mM NaOMe solution. This solution was prepared just before the reaction was started, to prevent oxidation of the phenol(ate), which occurs slowly under air. Experiments were performed by mixing 15 mL of each solution at room temperature, both under air and under a dinitrogen atmosphere (with degassed solutions). An experiment was also performed at −25 °C under a dinitrogen atmosphere, using an ethanol/dry ice bath. The resulting reaction mixture was 2 mM in copper, 4 mM in phenol and 2 mM in base, so, Cu:phenol:base = 1:2:1. It should be realized that these are not "normal" catalytic conditions. However, it was decided to use this low phenol concentration to make sure that all signals in the HPLC analysis would fall within the detection range. Furthermore, only methanol was used as the solvent. No toluene cosolvent was used, as this was found to result in a very large, interfering signal in the chromatogram close to the signal of the dimer phenol.

From the reaction mixtures, 0.5 mL samples were taken with a 1 mL syringe (under dinitrogen where applicable) and quenched by squirting these into a 10 mL volumetric flask containing a two-layer system of 0.02 M aqueous HCl (2 mL) and *n*-hexane (∼4 mL). After the flask was thoroughly shaken, it was topped up with *n*-hexane to 10 mL and shaken once again. After separation of the layers, part of the hexane layer was collected with a syringe and filtered through a disposable filter (0.45 μm). The filtered solution was injected into the HPLC system (20 μL). The data were collected and processed with a computer. The eluent coming off the column was monitored with a UV-absorbance detector at 195 nm. Test runs with equimolar mixtures of monomer and dimer DMP showed that the peak areas were the same at this wavelength, implying that at 195 nm the monomer and the oligomers have the same molar extinction coefficient. Alternatively, detection can be done at 280 nm where the $\pi-\pi^*$ transition of the aromatic rings is observed. At this wavelength the area of the dimer signal is twice that of the monomer signal. DMP oligomers up to the hexamer can be detected with the setup described, as shown in Figure 2, although the signal of the hexamer was generally too small and too broad to obtain reliable results.

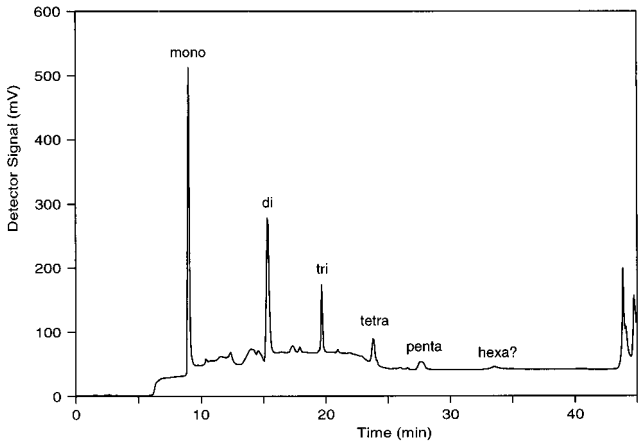

Figure 2. Typical HPLC chromatogram of a mixture of oligomeric phenols, obtained from redistribution of dimer DMP. UV detection at 195 nm.

As a reference, a solution of the dimer phenol and base, prepared as described above, was left standing for 10 min in air after mixing the phenol and base, which is the approximate time between preparing the solution and the starting of an experiment. To a 1 mL aliquot of this solution was added 3 mL of methanol. From the resulting mixture a 0.5 mL sample was obtained, and treated as described above for samples of reaction mixtures. HPLC analysis of this "blank" sample showed that next to the dimer signal, very small amounts of monomer and trimer DMP were already formed. Since such signals were absent in the chromatogram of the dimer DMP itself, it appears that in the blank already a small amount of the dimer has reacted. The total peak area of detectable phenols in this sample, corrected for the dilution of this solution with respect to reaction mixtures (i.e. by a factor of 2), amounted to 2.29×10^5 au, which was used as a reference value.

Experiments with Dimer Anisole. Experiments with the methyl ether of the dimer phenol, i.e. dimer anisole, were followed principally with ^{1}H NMR. Therefore, all reactions were carried out in deuterated chloroform, using a stock solution of 1 mmol of dimer anisole and 1 mmol of 4-*tert*-butyl-2,6-dimethylphenol (TBDMP) in 5 mL of $CDCl_3$. Then 1 mL samples from this solution were treated under an atmosphere of dinitrogen with small amounts of various reagents, like K_2CO_3, $K_2CO_3/Cu(Nmiz)_4(NO_3)_2$, and K_2CO_3/I_2. In all these cases heterogeneous systems were formed. Nevertheless, from test experiments with the dimer phenol it was found that such systems do give rise to oxidative coupling and/or redistribution reactions. All heterogeneous systems were filtered prior to analysis. To the samples of the solutions treated with iodine some powdered sodium thiosulfate was added to remove the iodine, prior to filtering. The samples obtained from the reactions with copper(II) (both under air and dinitrogen) were left standing under dinitrogen for several minutes after

filtering off the solid matter, to allow any copper(II) species that might have dissolved to be reduced to copper(I), so that the samples could be analyzed with NMR. In addition, several samples were also analyzed by HPLC, after dilution with methanol.

Results and Discussion

Reactions with the Monomer Phenol. HPLC analysis of samples of reactions under air started with monomer phenol revealed no information on the occurrence of oligomers during the reaction. Only the signal of residual monomer was observed, which decreased slowly over time. Also, a very small, almost negligible signal corresponding to the dimer phenol was observed. Nevertheless, a polymerization reaction did take place, as after some 20 min a white precipitate (PPE) was formed in the reaction mixture under air. Several other procedures for quenching the samples were tried, such as a lower acid concentration (just enough to neutralize the base cocatalyst) or a mixed treatment with sodium sulfide (to precipitate $Cu^{II}S$) followed by acid. None of these methods gave rise to signals of oligomers in the chromatograms. So, it appears that oligomeric phenols are present in at most very small, undetectable amounts.

When the same reaction was performed under an atmosphere of dinitrogen, once again a slow decrease of the monomer signal in time was observed. Only after relatively long reaction times (20 min) clear signals of dimer and trimer were observed. After even longer reaction times (3 h) a very small signal of the tetramer phenol had appeared, but still 85% of the amount of detectable phenols consisted of the monomer. No precipitate was formed, as one would expect since there is only enough copper(II) present to convert 25% of the phenol groups, and no reoxidation of copper(II) can occur in the absence of dioxygen.

The fact that no or only small amounts of dimer, trimer, and higher oligomers of DMP are obtained when starting the reaction with the monomer is likely to be caused by the higher reactivity of oligomeric phenols compared to the monomer. As described in an earlier publication,[17] in dioxygen-uptake experiments started with mixtures of monomer and dimer, a small but distinct preference for the dimer is observed in the oxidation reaction. It is quite likely that when some dimer DMP is formed during the reaction started with the monomer, this dimer will react swiftly to higher oligomers, thereby keeping the concentration of the dimer low. The same applies for the other oligomers. Apparently, this is especially the case when the reaction is performed under air, because then the catalyst is continuously regenerated and the reaction can proceed further to form high oligomers (and PPE), that cannot be detected with the current setup. It is noted again that in these experiments a DMP/Cu ratio of only 2 to 1 is used. Since normally a much higher DMP/Cu ratio is used,[15] the above course of reactions is not expected to contribute to a large extent during the initial stages of a reaction under normal conditions.

Reactions with the Dimer Phenol. Experiments started with pure dimer phenol were performed at room temperature, both under air and under dinitrogen, and also under dinitrogen at −25 °C. The results from the aerobic experiment are shown in Figure 3, expressed as percentages of the total peak area of the detectable oligomers in the reference sample. It is clear from this figure that, after adding the copper solution to the dimer/base solution, a very fast reaction occurs, during

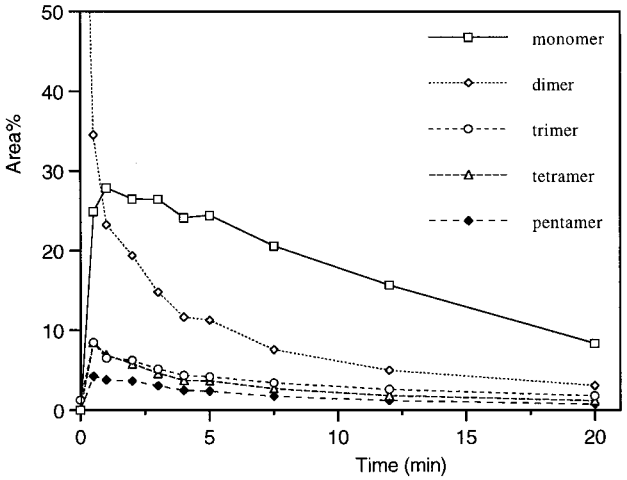

Figure 3. Peak areas of DMP oligomers from reaction of the dimer with base/Cu under air, expressed as percentages of the initial total peak area. Cu:Nmiz:dimer:base = 1:30:2:1; [Cu] = 2 mM; T = 293 K.

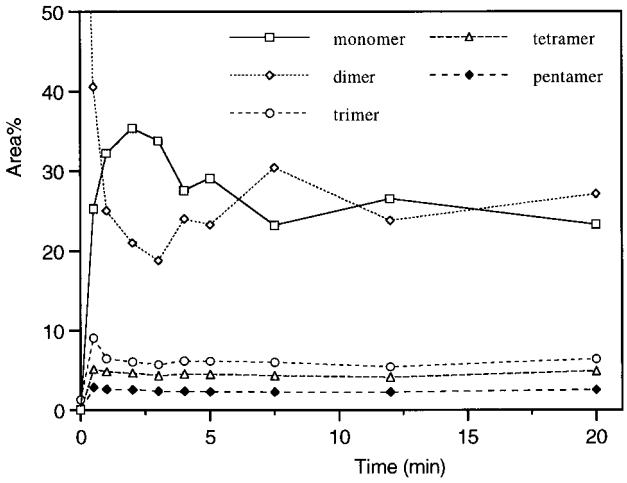

Figure 4. Peak areas of DMP oligomers from anaerobic reaction of the dimer with base/Cu, expressed as percentages of the initial total peak area. Cu:Nmiz:dimer:base = 1:30:2:1; [Cu] = 2 mM; T = 293 K.

which a relatively large amount of the dimer is converted into the monomer phenol. This reaction appears to be almost complete after only 30 s. Also, relatively small amounts of trimer, tetramer, and pentamer phenol are formed. Furthermore, it can be seen from Figure 3 that the oxidative coupling reaction takes place, as the amounts of the different oligomers slowly dwindle down, until after prolonged reaction time (4 h; not shown) only a very small monomer peak is detected. The relative amounts of the different oligomers remain constant after about 5 min. It appears that next to the oxidative coupling a very fast reaction is operative, whereby monomer phenol is formed as one of the products.

To exclude the oxidative coupling reaction as much as possible, the same reaction was performed under an atmosphere of dinitrogen, the results of which are shown in Figure 4. Some oxidative coupling will still take place, however, as the reaction is started with copper(II). Based on the stoichiometry of the reaction, two copper(II) ions are needed for one C−O coupling step regardless whether a radical or an ionic mechanism is operative, and assuming that there is no Cu(II) → Cu(0) reduction pathway. So, on the basis of the phenol/

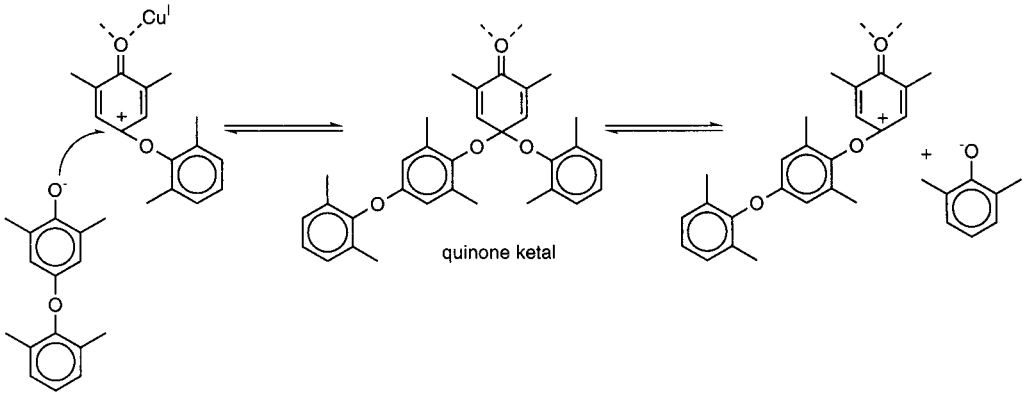

Figure 5. Redistribution of the dimer via a quinone ketal intermediate, shown for a heterolytic pathway, inside the coordination sphere of copper, as denoted by the dotted lines.

Cu ratio used in this experiment, 25% of the initial amount of phenol (ROH) groups will disappear due to the oxidative coupling reaction. Indeed a rapid decrease of the total peak area of the detectable phenols was observed to about 65% of the initial area during the first 3 min, after which this percentage remained constant. Assuming that 25% of the signal has disappeared due to oxidative coupling, which appeared to be the case since the blue color of the copper(II)/Nmiz complex had disappeared, this implies that the missing 10% must be due to formation of higher oligomers (and DPQ) that cannot be detected using this method. After a total of 4−5 min, the amounts of the different oligomers remain constant.

It is clear from the reactions started with dimer phenol, both under air and under dinitrogen, that some very fast reaction is operative, resulting in a relatively large amount of monomer phenol being formed. This phenomenon has already been reported before, and has been described by a mechanism featuring a quinone ketal intermediate.[23,26] The formation of such an intermediate was found to be the most likely possibility for the coupling of oligomeric phenols on the basis of quantummechanical calculations described in a recent publication.[22] Moreover, it appears to be the only pathway that can explain the formation of monomer DMP from the dimer, by decomposition of the intermediate ketal, as depicted in Figure 5. The basic idea in this pathway is that the formation of a quinone ketal, shown for a nucleophilic coupling pathway, is in fact reversible. The newly formed C−O bond may dissociate to reform two dimeric species, or the other ether bond may break to form a monomeric and a trimeric species. It is quite possible that this redistribution process may only occur as long as the quinone ketal remains coordinated to the copper complex, tentatively shown in Figure 5, as it can be envisioned that this coordination destabilizes the ether bonds of the ketal.

It has been uncertain whether homolytic (radical) or heterolytic (ionic) bond dissociation occurs. However, some educated guesses can be made. Since a relatively large amount of monomer phenol is formed, it seems that the monomer is something like a "dead end" in this reaction, in a relative sense: it appears to react only if there are (almost) no oligomers left (under the current conditions). It can easily be seen that, in general, the two ether bonds in a ketal are identical, unless one of the residues is a monomer. One of the main differences between the monomer and any oligomer is that the phenol moiety bears a *p*-phenoxy substituent in the latter case, which is a powerful (resonance) electron donor.[30] This electron-donating effect results in an increase in electron density in the phenolic residue, as is illustrated by the (slightly) lower acidity and better oxidizability of the dimer with respect to the monomer, as discussed elsewhere.[17] So, if a heterolytic fission pathway would be operative, as shown in Figure 5, the best leaving group is the one that best stabilizes the negative charge, which is the monomer, thereby giving rise to relatively large amounts of the monomer phenol. It is noted that a heterolytic pathway that would place a positive charge on the phenolic leaving group and a negative charge on the quinoid species is not very likely, since it is not in agreement with the existing charge distribution in a C−O bond ($C^{\delta+}$, $O^{\delta-}$) due to the difference in electronegativity between oxygen and carbon. This difference in electronegativity is also unfavorable for a homolytic fission mechanism, whereby radicals are formed. Furthermore, a radical pathway is not in agreement with the large amount of monomer formed, as it is known that monomeric radicals are very unstable and would react to give primarily DPQ.[31,32] Formation of large amounts of DPQ was not observed (visually). Also, a homolytic bond fission would mainly result in the formation of oligomeric phenoxyl radicals, since these are thermodynamically more stable than monomeric radicals. Finally, no radical species were observed in EPR spectra obtained from frozen samples of a reaction started with the dimer. Although the above discussion might seem somewhat tentative, the current results do point to a heterolytic mechanism.

Irrespective of the detailed, molecular mechanism of the ether bond fission, it is clear that the reaction does not end here, since a new reactive species is formed, as shown in Figure 5 by the quinoid cation. Such a species may react with another phenol, redistribute, etc. However, no net increase in the average degree of polymerization does result from this reaction. Since ultimately a polymer is formed, some complementary pathway must be operative. As such a pathway, the rearrangement of the quinone ketal has been proposed,[23,26] as drawn schematically in Figure 6. This rearrangement is a concerted process, in fact a Claisen rearrangement, which is a special case of sigmatropic transposition, as elaborated upon by Ionescu *et al.*[33] This rearrangement results in the quinone group being shifted over the backbone of the oligomeric species, until eventually the end is reached and a phenol is formed by tautomerisation of the hemiketal. It is clear that this process cannot take place within the coordination sphere of copper,

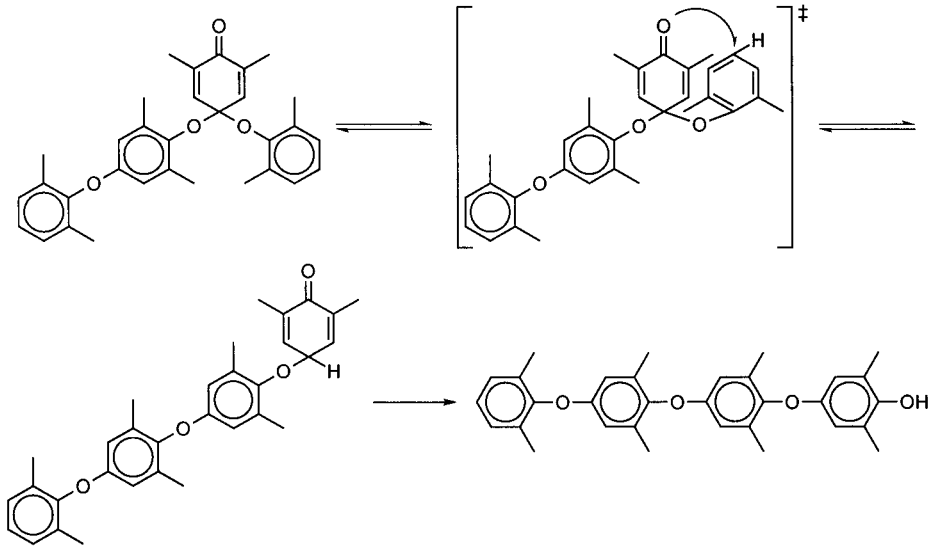

Figure 6. Schematic representation of the rearrangement of a quinone ketal, outside the coordination sphere of copper.

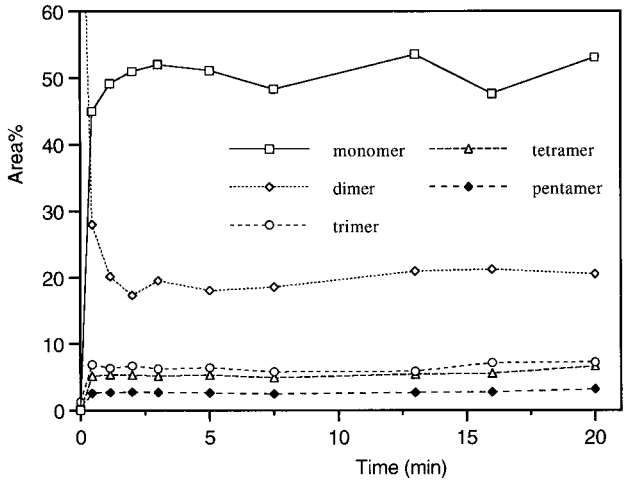

Figure 7. Peak areas of DMP oligomers from anaerobic reaction of the dimer at low temperature with base/Cu, expressed as percentages of the initial total peak area. Cu: Nmiz:dimer:base = 1:30:2:1; [Cu] = 2 mM; T = 248 K.

since the reaction involves the carbonyl head of the quinone ketal. It is therefore believed that the *redistribution* pathway is operative as long as the quinone ketal remains coordinated to the copper complex and that *rearrangement* will occur upon dissociation of the quinone ketal from the copper complex.

Although the measurements performed so far provide evidence for the redistribution reaction, no direct evidence for the rearrangement pathway has as yet been observed. It has been reported,[25,34] however, that the redistribution may be prohibited by performing a reaction at low temperatures, as the redistribution supposedly has a higher activation energy than the rearrangement because it involves bond breaking, whereas the rearrangement is a concerted process. It was shown from experiments starting with dimer phenol performed at −15 or −25 °C that mainly even-numbered species (tetramer and hexamer) were formed,[25,34] which is to be expected if rearrangement is the only pathway operative. Therefore, it was decided that the experiment performed at room temperature under an atmosphere of dinitrogen had to be repeated at −25 °C. The results of this experiment are shown in Figure 7.

A surprising result was observed. The monomer peak was found to be almost twice as high as in the experiment performed at room temperature, amounting to about 50% of the initial peak area. Apparently, the redistribution reaction was not inhibited at all at low temperature. However, according to the even higher amount of monomer observed, some other reaction must have been inhibited; this is also supported by the fact that now the total amount of detectable phenols after 3 min remains constant at 85% of the initial amount, indicating that not all copper has reacted. No clear explanation can be given for these observations at this time, although it can be envisioned that the quinone ketal will remain longer inside the copper coordination sphere at lower temperatures, leading to more extensive redistribution. This experiment was subsequently repeated at −45 °C, affording results (not shown) that were very similar to those obtained at −25 °C.

It has been reported that PPE itself can also be "redistributed" with DMP.[29,35] A better term in this case is probably "equilibrated"[36] since the rapid drop in molecular weight of the PPE is most probably due to a combination of redistribution and rearrangement reactions: in our opinion during these so-called "redistributions" a quinone ketal is formed first and then the quinone group will shift along the main chain by rearrangement and finally redistribution (=ether bond dissociation) from a random position of the quinone can take place. According to our current proposal, this implies that the quinone ketal has to dissociate from the copper ions for rearrangement, recoordinate to copper for dissociation (redistribution) and re-formation of the quinone ketal, dissociate again for rearrangement, etc. etc. So, for a swift equilibration of PPE with DMP or a lower oligomer, the quinone ketal needs to dissociate from copper and recoordinate to copper multiple times. This may seem not very likely, since the copper(I) species will be reoxidized very fast by dioxygen, after dissociation of the quinone ketal, and re-enter the catalytic cycle. However, previous experiments[37] have shown that even during the most active phase of the reaction, some 40% of the initial amount of the catalyst is present as the copper(II) catalyst precursor (according to EPR) or some other inactive species. Therefore, at any given time, enough copper (as Cu^{II}), which is not engaged in the catalytic cycle, is available for the

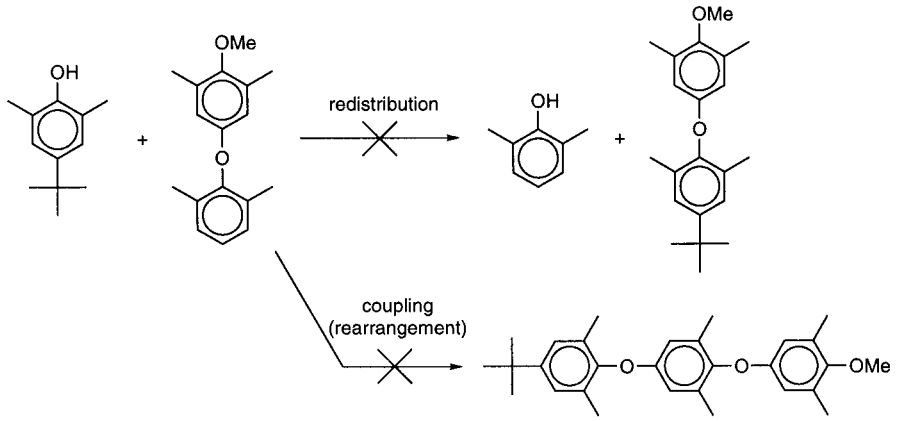

Figure 8. Representation of the (forbidden) redistribution and rearrangement reactions between TBDMP and dimer anisole.

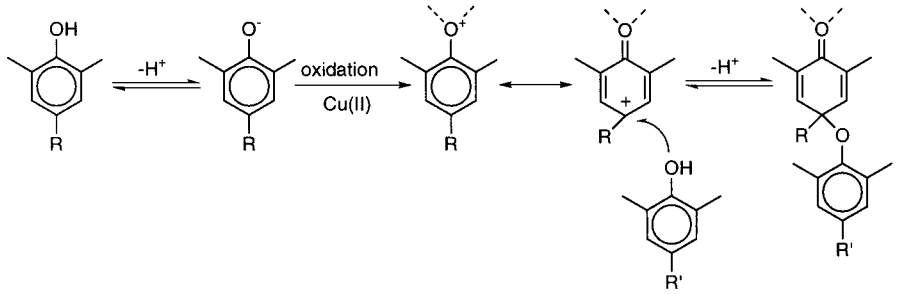

Figure 9. Schematic representation of the formation of a quinone ketal. Coordination to copper is denoted by dotted lines. R, R′ = H or R−PhO.

quinone ketal to coordinate to. So, repeated dissociation/recoordination of a quinone ketal from-and-to copper is very feasible.

Reactions with the Dimer Anisole. Phenols other than DMP can also be used for equilibration with PPE,[35,36,38] thereby offering the possibility of preparing polymers with a variety of differently substituted terminal phenoxy moieties. One example is the equilibration of PPE with 4-*tert*-butyl-2,6-dimethylphenol (TBDMP), a reaction that can take place by just stirring a solution of PPE and TBDMP in toluene at room temperature for several hours, without any initiator added. The TBDMP is consumed during the reaction and was shown to be incorporated as tail unit in the resulting oligomeric product.[38] Although these equilibrations occur readily with phenolic species, it has been reported in the literature that species with a methylated phenol group (anisoles) are not reactive.[27,28]

To study the reactivity of methylated species with the reactive TBDMP, an experiment was performed with the methyl ether of dimer DMP: 4-(2′,6′-dimethylphenoxy)-2,6-dimethylanisole, or dimer anisole. An equimolar mixture of dimer anisole and TBDMP in $CDCl_3$ was studied under various conditions, to check whether one of the reactions, redistribution or oxidative coupling (by rearrangement), as shown in Figure 8, does occur. TBDMP was used as it facilitates analysis of the reaction mixtures by NMR, because of the *tert*-butyl substituent and because it is known to be very active in redistribution reactions.[38]

Several reaction conditions were applied. First the possible "spontaneous" redistribution was investigated by stirring the solution for 2 days under an inert atmosphere. No reaction had occurred. Samples of this solution were then treated with several reagents: base (K_2CO_3), base/$Cu(Nmiz)_4(NO_3)_2$ and base/iodine (all heterogeneous systems) under an atmosphere of dinitrogen. Again, no reaction had taken place, according to NMR and HPLC analysis of the samples. Finally, an experiment was performed where a sample of the solution was stirred under air for several hours with base/$Cu(Nmiz)_4(NO_3)_2$. In this case, some reaction had occurred according to NMR and HPLC; however, it was found that this was due excusively to oxidation of TBDMP. So, dimer anisole is obviously inactive in either the redistribution or the oxidative coupling (rearrangement) reaction. It was reported by van Aert et al. that oxygen-methylated PPE was found also to be inactive in the equilibration attempts.[39]

The fact that no equilibration with the dimer anisole had occurred is in agreement with the quinone ketal mechanism. As schematically shown in Figure 9, both species need to be deprotonated before the quinone ketal is formed, and thus phenols are required. The first species must be deprotonated prior to coordination to the copper catalyst, followed by oxidation (shown for an ionic pathway), and the second one must be deprotonated to form the ether bond. So, it is clear that the formation of a ketal can only occur at the *para*-position of the phenolic "head" of an oligomeric or polymeric species.

Conclusions

Reaction mixtures of reactions started with either the monomer DMP or the dimer analyzed by HPLC, have provided important information on the course of the polymerization reaction. In the case of monomer phenol, no oligomers could be detected when the reaction was performed under air, and only very small amounts were observed when the reaction was performed under a dinitrogen atmosphere. When the reactions were started with dimer phenol, either under air or under dinitrogen, relatively large amounts of monomer phenol were found

to be formed rapidly, whereas the amounts of the different oligomers were relatively low. These observations have been explained by the higher reactivity of oligomeric phenols compared to the monomer. So, dimer and other oligomers rapidly react away, leaving monomer DMP in solution.

The observation that monomer phenol was formed during reactions started with the dimer has been explained by a pathway featuring a quinone ketal intermediate. This ketal may either decompose into two new species (redistribution) or rearrange to afford (ultimately) one polymeric phenol. It is assumed that the redistribution may only occur while the quinone ketal remains coordinated to the copper catalyst, whereas the rearrangement will occur outside the coordination sphere of copper. Some evidence was found that the redistribution reaction might proceed via heterolytic fission of one of the ether bonds. Performing the experiment at −25 °C resulted in even more monomer phenol formed, which is as yet not clearly understood and merits a further investigation, to obtain a better understanding of this behavior.

It was furthermore shown that the methyl ether of dimer phenol, dimer anisole, does not undergo either redistribution or rearrangement reactions, which is in agreement with the quinone ketal mechanism which requires that both species, which are to be coupled, can be deprotonated. Coupling between an oxidized species and a phenol or phenolate can only occur at the *para*-position of the head phenolic ring of the former species, and not on an internal phenyl ring.

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