Mechanistic studies of the oxidative coupling polymerization of 2,6-dimethylphenol: 4. Mechanism of polymer formation catalysed by a copper(II)–tmed complex*

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A catalytic cycle is described starting from a chloro-bridged dinuclear copper–tmed‡ complex as the catalyst in the oxidation of 2,6-dimethylphenolate anions to 2,6-dimethylphenoxonium intermediates. The effect of strong base, known to accelerate the reaction, is to deprotonate 2,6-dimethylphenol (DMP) to yield its far more reactive anion. In the whole catalytic cycle dioxygen is subsequently reduced to water (i.e. in total a transfer of four electrons is involved). It appeared to be essential to use an excess of amine to obtain a maximum amount of highly active and highly specific catalyst for polymer formation. The fixed product composition obtained under the proper polymerization conditions (C–O coupling yielding polymer *versus* C–C coupling yielding DPQ§) originates from the reaction of the phenoxonium intermediate with complexed DMP. Coupling of the highly favoured form of complexed DMP (which has a partial negative charge on oxygen) with C4 of the phenoxonium intermediate yields C–O coupled products. The inevitable formation of a small amount of C–C coupled DPQ (in our solvent system at 25°C, about 3%) results from the reaction of the highly unfavoured structure of DMP (which has a partial negative charge at C4) with the phenoxonium intermediate at its C4 position.

(Keywords: 2,6-dimethylphenolate anion; polymerization conditions; two-electron transfers; phenoxonium intermediate)

INTRODUCTION

Hay discovered the very important industrial oxidative coupling polymerization of 2,6-dimethylphenol (DMP), giving poly(2,6-dimethyl-1,4-phenylene oxide) (PPO) generally in high yield and of high molar mass[1,2]. Formation of small quantities of the undesired diphenoquinone cannot, however, be avoided (*Scheme 1*). Because of the outstanding properties of the polymer and its commercial importance many workers have investigated this reaction[3–16].

Copper–amine complexes are known to be excellent catalysts in the oxidative coupling polymerization of phenols. The chloro-bridged dinuclear copper–tmed complex proved to be a good catalyst precursor in the polymerization of DMP. This catalytic system has been used by us in experimental studies on the mechanism of oxidative coupling polymerization[17–22]. The present paper describes our views on this mechanism.

SUMMARY OF OUR PREVIOUS RESULTS AND SOME RECENT EXPERIMENTAL OBSERVATIONS

This section gives an overview of the most important experimental results, leading to a mechanism for the oxidative coupling polymerization of DMP catalysed by copper complexes prepared from $CuCl_2$ and tmed.

To obtain a maximum amount of the very active dinuclear copper catalyst having an N/Cu ratio of 2, at least a fivefold excess of tmed is needed, as was shown by both u.v./vis and electron paramagnetic resonance (e.p.r.) spectroscopy[19]. Once the maximum amount of this complex is formed, further addition of tmed neither enhances reaction rates nor shortens induction times[17]. Also, the final specificity of the reaction towards PPO formation is not affected by N/Cu for $\text{tmed/Cu} \geqslant 5$ [18]. At low N/Cu a considerable amount of mononuclear-copper complex is present[19], yielding finally up to 45% DPQ[18]. Therefore, the mechanism for the oxidative coupling polymerization of DMP was further studied under 'proper' reaction conditions ($\text{N/Cu} > 10$).

The active catalyst is initially formed from a chloro-bridged dinuclear copper complex, while hydroxide is needed as a 'co-catalyst' for the formation of phenolate anions[17]. The shorter induction time and higher initial

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[*] Part 1: see Reference 17. Part 3: see Reference 19

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[‡] Tmed, *N,N,N′,N′*-tetramethylethylenediamine

[§] DPQ, 4-(3,5-disubstituted-4-oxo-2,5-cyclohexadiene-1-ylidene)-2,6-disubstituted-2,5-cyclohexadiene-1-one

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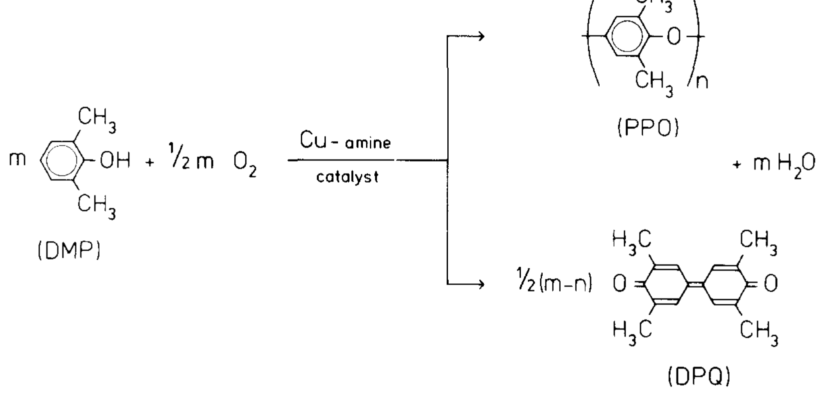
Scheme 1



rate when starting directly with phenolate support this conclusion. Initial rates were found to be only slightly lower when half of the hydroxide was added to the catalyst solution and half to the DMP solution. If all the hydroxide is first added to the copper–tmed solution, an excess of hydroxide destroys the catalyst, so the highest catalytic activity is found at ~OH/Cu ≈ 1.

Copper-amine complexes prepared from $CuCl_2$ and $CuBr_2$ yield very active catalysts for oxidative coupling[20]. In contrast, copper–tmed complexes with weakly coordinating (NO_3^-) and non-coordinating (ClO_4^-, $CF_3SO_3^-$ and BF_4^-) counterions show almost no activity. The use of coordinating counterions (Cl^- or Br^-) is essential to obtain a dinuclear complex. The optimum catalytic activity is found at OH/Cu ≈ 1 for $CuCl_2$ and $CuBr_2$, whereas copper salts of weakly and non-coordinating counterions require OH/Cu ⩾ 2. Although very large differences in catalytic activity were observed, no effect on the final specificity was found: ≈3.5% DPQ and ≈96.5% PPO for all copper salts at high N/Cu.

The reaction rate was found to follow a first-order rate dependence on catalyst concentration[17]. The Lineweaver–Burk plot of R_0^{-1} *versus* $[DMP]_0^{-1}$ yields straight lines, intersecting the *y*-axis[17]. Therefore, a kinetic scheme for Michaelis–Menten type behaviour is required to describe the kinetics of the oxidative coupling polymerization of DMP. However, neither catalyst concentration nor DMP concentration affect the final specificity[18].

Under proper polymerization conditions the factors that have an effect on the final C–C *versus* C–O coupling ratio were found to be reaction temperature and solvent polarity[21]. With increasing reaction temperature and increasing solvent polarity the yield of DPQ did increase.

To investigate whether para-chlorination of DMP might be a possible reaction step, some experiments were performed with stoichiometric amounts of DMP and $CuBr_2$: $[DMP] = \frac{1}{2}[CuBr_2] = 0.015$ M, OH/Cu = 1 and N/Cu = 30. Analysis of the product mixture by gas chromatography (g.c.), i.r. and ultraviolet (u.v.) did not indicate any formation of 4-bromo-2,6-dimethylphenol. Moreover, it appeared that substitution of 10–30% DMP by 4-bromo-2,6-dimethylphenol under standard catalytic conditions gave only lower dioxygen consumption rates and no improvement of specificity. Finally, addition of LiCl up to Li/Cu = 6 to a reaction mixture under standard catalytic conditions did not result in rate enhancements. So the maintenance of chloro- or bromo-bridged dinuclear copper complex as precursor for the active catalyst as pointed out above seems to be the only role of the halides under the present reaction conditions.

DISCUSSION

For convenience a schematic representation of the catalytic cycle to be discussed is given in *Scheme 2*.

Copper complex composition (complex I in scheme 2)

The catalyst precursor in the oxidative coupling of DMP, using tmed as ligand and $CuCl_2$ as source for copper ions, is a dinuclear chloro-bridged complex containing one tmed ligand per copper ion. Data on the crystal structure of this complex show a square pyrimidal geometry around copper[23].

However, from a combination of the kinetic and spectroscopic data it becomes clear that at least a fivefold excess of tmed is necessary to obtain a maximum amount of the active catalyst. Therefore, the mechanism described here applies to a situation where N/Cu ⩾ 10. Under these conditions complex I (*Scheme 2*) is the only one that plays a significant role in the reaction. The use of mineral base generally accelerated the reaction. Addition of hydroxide to complex I yields a dinuclear hydroxo-bridged complex. Structure analysis showed that this complex is essentially square planar[24]. However, as will be shown in the next section, added hydroxide is primarily used for the formation of phenolate anions rather than hydroxide bridges.

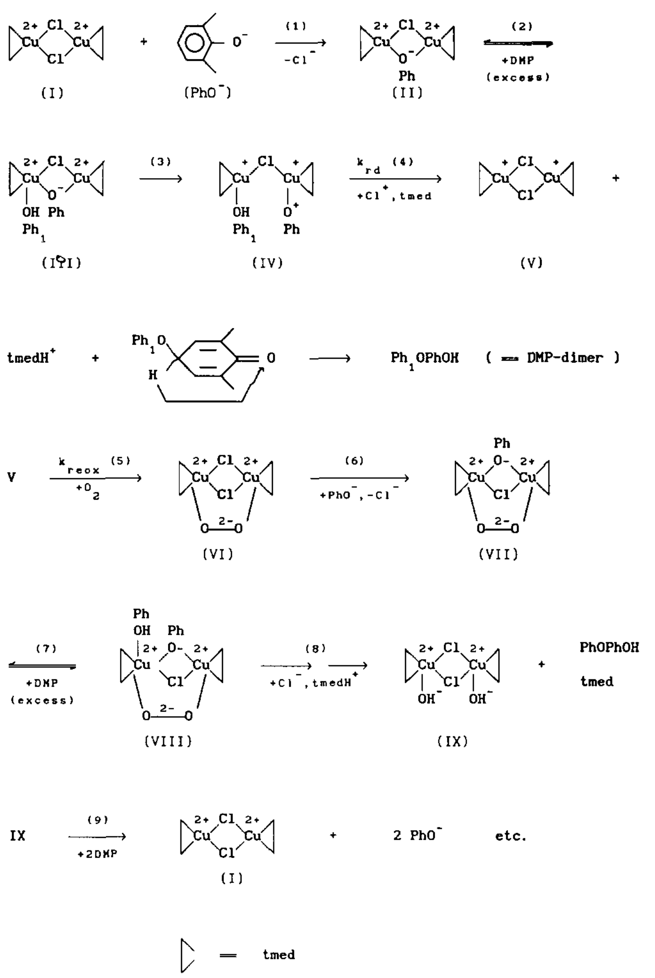
Reaction with DMP (oxidation)

The role of hydroxide in the catalytic process has been investigated extensively. Its role was determined to be that of the so-called co-catalyst. Reaction of hydroxide with DMP yielded the strongly coordinating phenolate anion, whereas neutral DMP itself is only weakly coordinating. This is in line with Gampp and Zuberbühler who stated that deprotonation of the substrate is a logical first step[25]. This idea was supported by several authors describing the oxidative coupling reactions of phenols[26–31].

When the reaction was started by the addition of phenolate anions to a chloro-bridged copper complex, significantly shorter induction times, defined as the time between mixing of the reactants and the moment dioxygen consumption starts, were found than when DMP was added to the preformed hydroxo-bridged complex. For a hydroxo-bridged complex hydroxide has to be liberated by chloride before it can form reactive phenolate anion. Since this rearrangement in copper coordination requires more time, longer induction times are found.

Further evidence for chloro- or bromo-bridged copper complexes as active catalyst precursors was obtained

Scheme 2



from experiments using copper salts of weakly or non-coordinating counterions (NO_3^-, ClO_4^-, $CF_3SO_3^-$ and BF_4^-). These salts give oxidation rates that are up to fifty times lower than those obtained for chloro- or bromo-bridged complexes. In these systems strongly coordinating hydroxide cannot be replaced by DMP. Only if DMP anions are added to compete with the bridging hydroxide (i.e. raising the OH/Cu ratio from 1 to 2) is a tenfold increase in reaction rate observed. All these observations have been used in developing the catalytic cycle of *Scheme 2*, by presenting the chloro- (or bromo-) bridged copper complex as starting catalyst or precursor (complex I), which reacts in step 1 with phenolate to give a phenoxo-bridged complex II.

Under normal conditions using $CuCl_2$ or $CuBr_2$ and OH/Cu = 1, the reaction follows Michaelis–Menten type kinetics in DMP independent of addition of base to catalyst or substrate. Therefore, coordination of DMP to the catalyst (at an axial position) has to be a reversible process as shown in *Scheme 2* (reaction step 2). Coordination in axial position is probably far more favourable for a DMP unit than for a phenolate anion. Furthermore, axial coordination of phenol is known to be a fast ligand exchange process, as is required for Michaelis–Menten type kinetics. Reaction step 2 is followed by the rate-determining steps 3 and 4 involving deprotonation of coordinated DMP by the excess of tmed and formation of DMP-dimer. The electron deficient phenoxonium unit is liable to leave its coordination site and to react with the neighbouring deprotonated DMP-unit.

Reoxidation of the copper(I) complex V was always faster since the dioxygen pressure was kept high enough to avoid the reaction rate becoming dependent on the dioxygen pressure.

In studying phenoxo-bridged dinuclear copper(II) complexes, ligands have been synthesized in which the phenoxide is covalently linked to the amine ligand. This ligand then contains four or six coordinating tertiary nitrogens. Crystal structures of dinuclear copper(II) complexes with one phenoxo- and one hydroxo-bridge have been reported[32–39]. As an example, the structure studied by Karlin *et al.* is shown below in *Formula 1*[33,34]. Structures of dinuclear copper(II) complexes with two phenoxo-bridges have also been extensively investigated[40,41]. An example studied by Gagné is shown in *Formula 2*. Complex II in *Scheme 2* has a structure similar to that in *Formula 1* and is used as a possible intermediate in the catalytic oxidation of DMP.

Reaction with dioxygen (reoxidation)

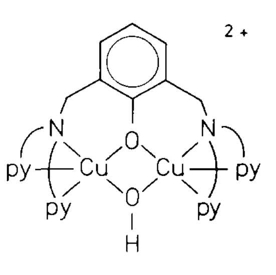
To oxidize copper(I) to copper(II) dioxygen is needed as electron acceptor. Copper(I) complexes are known to coordinate dioxygen[33,34].

In our investigations no real reoxidation rates could be measured. If real reoxidation rates are to be determined the reaction rate has to be independent of the phenol concentration. Therefore, since Michaelis–Menten kinetics are valid, very high DMP concentrations would be needed, subsequently giving rise to very high dioxygen consumption rates. Under those conditions, diffusion of dioxygen into the reaction medium will become rate limiting. Nevertheless, the fact that the reaction rate shows a linear relationship with low applied dioxygen pressures gives an indication that a first-order dependence on dioxygen concentration is valid. This is shown in *Figure 1* for dioxygen pressures <100 kPa. When the copper(II) chloride concentration is raised from 1.5×10^{-3} to 3.32×10^{-3} mol dm^{-3} (an increase by a factor 2.3) the slope increases by a factor 2.2, indicating a first-order rate dependence on catalyst concentration. Therefore, the following relationship holds (complex V refers to *Scheme 2*):

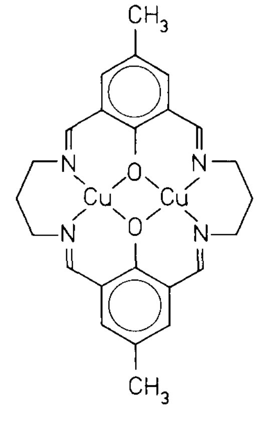
$$R_0 = k_{\mathrm{obs}}[\mathrm{CuCl_2}]p_{\mathrm{O_2}} = k_{\mathrm{reox}}[\mathrm{V}][\mathrm{O_2}]$$

Oxidation reactions of copper(I) complexes have been extensively studied[42,43]. These studies show a first-order rate dependence on dioxygen concentration and either

Formula 1



Formula 2



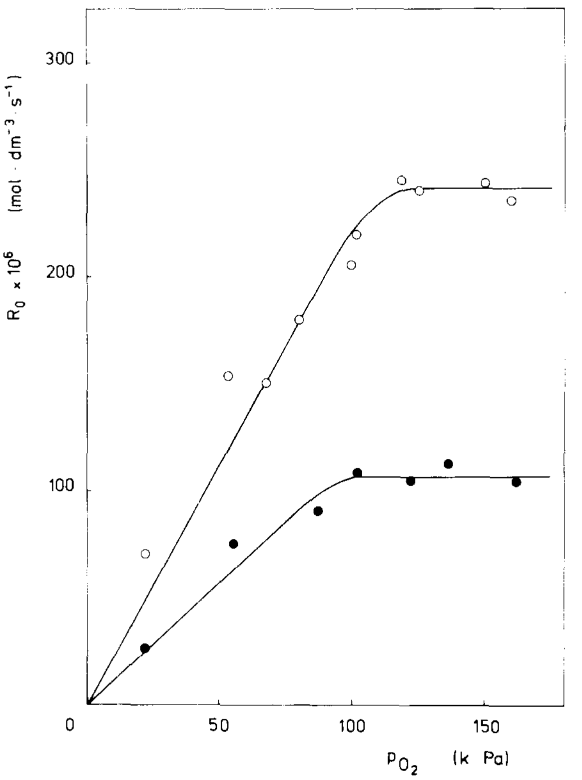


Figure 1 Initial reaction rate as a function of applied dioxygen pressure with OH/Cu = 1 and N/Cu = 10: ●, $[CuCl_2] = 1.5 \times 10^{-3}$ M; ○, $[CuCl_2] = 3.32 \times 10^{-3}$ M; T = 298.2 K, [DMP] = 0.06 M, solvent mixture 1,2-dichlorobenzene/methanol = 13/2 (v/v)

first- or second-order on copper concentration. Since the system investigated here deals with a dinuclear copper complex, this explains the first-order rate dependencies with respect to dioxygen pressure as well as copper concentration. As described by Karlin *et al.*, a dinuclear phenolate-bridged copper(I) centre can react with dioxygen to give a stable peroxo- phenolate-bridged copper(II) compound[33,34]. The reaction scheme is given below (*Scheme 3*).

Several similar reactions between dinuclear copper(I) complexes and dioxygen to give copper(II) complexes have been described[44,45]. Furthermore, *Scheme 3* has also been used in descriptions of the dioxygen binding sites of biological systems[46,47]. Therefore, reaction *Scheme 3* proposed by Karlin *et al.* seems possible in our proposed catalytic cycle as presented in *Scheme 2*.

In line with Karlin's results dioxygen can coordinate to structure V in *Scheme 2* and a subsequent very fast two-electron transfer gives the dinuclear copper(II) complex with a peroxo-bridge (structure VI). Oxidation of the second phenolate anion in reaction step 8 of *Scheme 2* results in complex IX and dioxygen is finally reduced to $2OH^-$ ions. So, in one catalytic cycle, two phenolate anions are oxidized to two phenoxonium intermediates. These phenoxonium units yield the coupling products.

In *Scheme 2* the dioxygen is coordinated as a two atom bridge; this appears from the literature to be the most probable one, though a μ-1,1-$[O_2]^{2-}$ structure cannot be excluded[47]. This structure may be preferred in protein structures with a short and fairly fixed Cu–Cu distance. In inorganic coordination compounds such as the present catalyst, no such preference is likely to be present, so no *a priori* conclusions about the CuO_2Cu unit can be drawn.

In the formation of structure VI in *Scheme 2* the dioxygen has accepted only two electrons. Since in the oxidative coupling polymerization of DMP one mole of dioxygen is reduced to two moles of water, an overall transfer of four electrons to dioxygen clearly takes place. Three possible schemes have been put forward for this process[48]:

(1) four one-electron transfer steps, of which the first electron transfer is highly unfavourable due to the low redox potential of -0.27 to -0.30 V[11,49–51]. This first step leads to the formation of an O_2^- ion, also known as superoxide. Indeed Thompson describes the reaction of a copper(I) complex with dioxygen at low temperatures yielding a stable copper(II)–superoxide complex[44];

(2) two two-electron transfer steps which are faster than (1); and

(3) a synchronous four-electron transfer step, which is faster than (2). However, in a dinuclear catalyst this would require reduction of copper(II) to copper(0). So far, no evidence for the existence of either a Cu(III) or a Cu(0) intermediate in the oxidative coupling of phenols is given in the literature[25].

Therefore, route (2) seems to be the most probable one. This was also suggested by e.g. Kaneko *et al.*[9], Schouten *et al.*[52] and Koning *et al.*[53]. So O_2^{2-}, after protonation, has to accept two more electrons in a single step. These electrons are obtained by oxidizing the second bridging phenolate anion in step (8), yielding the dinuclear copper(II) complex IX. After elimination of two OH^- ions complex I is regenerated and two new phenolate anions are formed. So a new catalytic cycle can start again at this point.

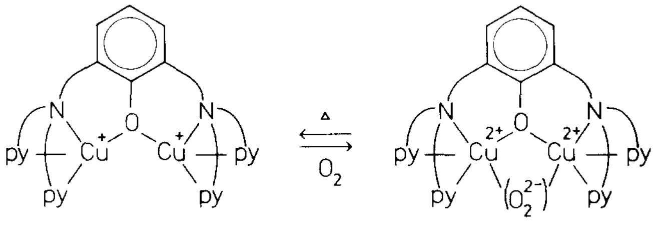
So, per catalytic cycle, two phenoxonium intermediates are formed that have to react to give either the PPO dimer or the undesired side product DPQ, as will be discussed in the next section.

Coupling mechanism

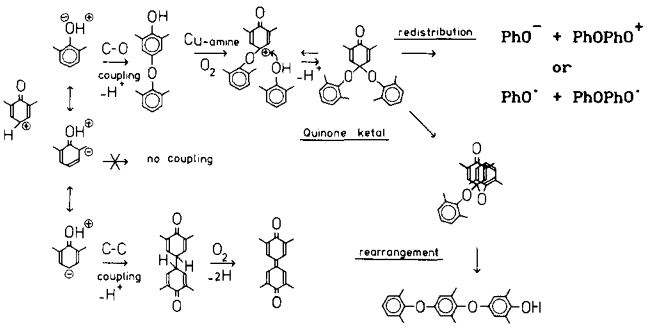
Our earlier experiments mentioned above showed that the catalyst itself no longer determines the C–O/C–C coupling ratio when proper reaction conditions are used[18–22]. A free radical combination, using a peroxide initiator, is known to yield finally 60–70% DPQ[54,55], instead of 3% under the present conditions. Therefore, an ionic mechanism is proposed, which also accounts for the formation of small amounts (<0.2%) of typical side products other than DPQ, e.g. 2,6-dimethyl (hydro)-quinone and 4-methoxy-2,6-dimethyl quinone, as described in the literature[15,56–59].

An ionic mechanism has already been proposed by Kresta *et al.*[13,14,60]. In the Kresta mechanism DPQ formation is proposed to result from a radical scheme, as we reported for low N/Cu ratio[18]. In the present mechanism, for proper polymerization conditions shown

Scheme 3



Scheme 4



in *Scheme 4*, both PPO dimer and DPQ are formed by an ionic mechanism. The 2,6-dimethylphenoxonium intermediate readily reacts with coordinated DMP. C–O coupling results from the reaction of a 2,6-dimethylphenol having a partial minus charge at the oxygen with the *para* position of the aromatic ring of the 2,6-dimethylphenoxonium unit. DMP can also have small partial minus charges at *ortho* and *para* positions of the aromatic ring. Due to the methyl substituents on the *ortho* positions, no reaction can occur at these positions. Combination of C4 of DMP with the phenoxonium unit yields C–C coupling followed by further oxidation to DPQ (as indicated in *Scheme 4*). Taking the high electronegativity of oxygen into consideration, the transition state with DMP with a minus charge at the oxygen is the most favoured. This is in line with the higher specificity for PPO formation.

As is shown in other publications in this series, amine concentration[18–21] (when no longer affecting the complex composition), amine structure[21], copper counterion[20], catalyst concentration[18] and 2,6-dimethylphenol concentration[18] do not affect specificity. Obviously, the product composition is merely determined by the difference in reactivity and contribution of the two dipolar transition state structures of DMP, as discussed above, and therefore also by the reaction temperature and the solvent type[21]. Indeed, lower temperatures and lower solvent polarity suppress C–C coupling[21].

In our catalytic cycle two DMP anions are oxidized in a dinuclear complex to phenoxonium cations, so a four-electron transfer is required. In this way dioxygen can be reduced to water in just one cycle, the low potential of $O_2^{2-} \rightarrow O_2^{4-}$ supporting this idea.

If coupling of DMP with a PPO-oligomer phenoxonium cation takes place in a copper coordinated state, the resulting neutral quinone–ketal intermediate, as shown in *Scheme 4*, has to leave the coordination site to give rearrangement.

Formation of long PPO chains occurs as shown in *Scheme 4*. Reaction of a PPO-cation with a PPO-chain or DMP yields a quinone-ketal intermediate, which gives redistribution or rearrangement, as discussed in the literature[61–67]. The redistribution gives no increase in average molar mass of the polymer, schematically represented by

$$\mathrm{S}_n^+ + \mathrm{S}_m \leftrightharpoons \mathrm{S}_{n-1}^- + \mathrm{S}_{m+1}^+ \quad (+\mathrm{H}^+)$$

or

$$\mathrm{S}_n^+ + \mathrm{S}_m \rightleftharpoons \mathrm{S}_{n-1}^{\bullet} + S_{m+1}^{\bullet} \quad (+\mathrm{H}^+)$$

Formation of high molar mass polymer can be explained by the quinone–ketal rearrangement mechanism:

$$\mathrm{S}_n^+ + \mathrm{S}_m \rightarrow \mathrm{S}_{n+m} \quad (+\mathrm{H}^+)$$

Chain extension with one monomer results when a phenoxonium cation (PhO^+) reacts with a PPO-chain, comparable to the simple C–O coupling route given in *Scheme 4*:

$$\mathrm{PhO}^+ + \mathrm{S}_n \rightarrow \mathrm{S}_{n+1} \quad (+\mathrm{H}^+)$$

However, it will be reported later[22] that the oxidation of PPO–oligomer proceeds faster than that of DMP. So, the rearrangement reaction

$$\mathrm{S}_n^+ + \mathrm{DMP} \rightarrow \mathrm{S}_{n+1} \quad (+\mathrm{H}^+)$$

must also contribute.

A reaction of the PPO-cation with C4 of DMP is highly unlikely for steric reasons. So in this scheme no additional DPQ is formed directly from PPO chains.

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