Studies on Immobilized polymer-bound imidazole copper(II) complexes as catalysts
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Chapter 6

Preparation of Telechelics by Oxidative Coupling Copolymerization of 2,6-Dimethylphenol with Tetramethyl Bisphenol-A Catalyzed by Copper(II) Complexes of N-methylimidazole

Abstract: A series of copolymerizations of 2,6-dimethylphenol (DMP) with 2,2-di(4-hydroxy-3,5-dimethylphenyl)propane (tetramethyl bisphenol-A, TMBPA) catalyzed by N-methylimidazole copper(II) complexes in toluene/methanol (12/3 v/v) was performed with TMBPA/Cu=1. The main product α,ω-bis(2,6-dimethylphenol)-poly(2,6-dimethyl-1,4-phenylene oxide) (PPO-20H) was characterized by $^1$H-NMR spectroscopy and GPC. It consisted of PPO-type telechelics carrying two hydroxyl end groups with $M_n$ in the range of 3400-5000 g/mol and $M_w/M_n$ ratios about 1.5. The formation of side products, i.e. homopolymer poly(2,6-dimethylphenylene oxide) (PPO) and 3,3',5,5'-tetramethyl-4,4'-diphenoquinone (DPQ), could be suppressed by slowly adding the DMP to the reaction system. A likely phenoxonium intermediate mechanism is derived from this copolymerization study.

6.1 Introduction

The synthesis of PPO-type telechelics with two hydroxyl end groups (PPO-2OH), a potential precursor for the preparation of block copolymers like polyesters [1,2], has been accomplished by means of White's method [3], electro-oxidative polymerization [4], electrophilic condensation reaction [5], pyridine-type copper(II) complexes as catalysts [5,6] and phase transfer catalyzed polymerization [7]. In general, a radical-radical mechanism or a radical-anion mechanism was presented to explain the formation of PPO-2OH, depending on the type of reaction system [3-7].

Recently, we systematically investigated the oxidative coupling polymerization of DMP catalyzed by imidazole-based copper(II) complexes [8-11] and proposed a possible mechanism via a phenoxonium intermediate [12].

The goal of this communication is to describe a synthetic procedure for the preparation of PPO-2OH based on oxidative coupling polymerization catalyzed by N-methylimidazole copper(II) complexes (Cu(II)-NMIm). It involves the copolymerization of DMP with small amounts of the bifunctional TMBPA (Scheme 1).

6.2 Experimental

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6.2.1 Materials

$\text{CuCl}_2(\text{H}_2\text{O})_2$ was obtained analytically pure from Merck. N-methylimidazole (NMIm) (Aldrich) was distilled from KOH under reduced $N_2$ pressure. DMP (Aldrich) was purified by repeated recrystallization from n-hexane. KOH, toluene (dried over Na) and methanol (Uvasol quality) were from Merck and used without further purification.

\[
\begin{align*}
\text{(m+n)} & \quad \text{CH}_3 \quad \text{CH}_3
\end{align*}
\]

\[
\begin{align*}
\text{(DMP)} & \quad \text{catalysts} \quad \text{(TMBPA)}
\end{align*}
\]

\[
\begin{align*}
\text{H-(-O-)}_{a-0-} & \quad \text{C-} \quad \text{O-(-O-)}_{m-a-}\text{H} \quad \text{CH}_3 \\
\text{PPO-20H}
\end{align*}
\]

\[
\begin{align*}
\text{H-(-O-)-H} & \quad \text{0=} \quad \text{=0}
\end{align*}
\]

\[
\begin{align*}
\text{PPO} & \quad \text{(DPQ)}
\end{align*}
\]

Scheme 1

6.2.2 Synthesis of TMBPA

TMBPA was prepared in terms of a literature procedure [13]. The obtained white crystals were characterized by elemental analysis (calculated for $C_{19}H_{24}O_2$: C, 80.2; H, 8.5; found: C, 80.3; H, 8.6) and $^1$H-NMR: 1.60 (s, $-C(CH_3)_2-$, 6H); 2.21 (s, Ph-CH$_3$, 12H); 4.50 (s, Ph-OH, 2H); 6.84 (s, Ph-H, 4H).
6.2.3 Techniques

$^{1}$H-NMR spectra (300 MHz) were recorded on a Varian 300 NMR Spectrometer. GPC measurements were performed on a Waters 150-C ALC/GPC Instrument, using THF as solvent (1 ml/min, 32 °C). The eluent was monitored by refractive index and a calibration plot was constructed with polystyrene standards.

6.2.4 Preparation of PPO-20H

Scheme 2 illustrates a procedure for the synthesis and isolation of PPO-20H, which was derived from our mechanistic insights into the present oxidative coupling copolymerization of DMP with TMBPA. The copolymerization reactions were carried out in a three-necked flask, equipped with a septum stopper and a magnetic stirring bar, under $O_2$ atmosphere. DMP dissolved in toluene was slowly added to the reacting system by a perfusor syringe injector at a constant rate. The used standard conditions were: $CuCl_2$= PhO$^-$ = TMBPA= 1 mmol; NMIIm/Cu=30; solvent mixture, toluene/methanol (12/3 v/v); total reaction

\[
\begin{align*}
30 \text{ mmol NMIIm} & \quad 1 \text{ mmol CuCl}_2 \\
& (\text{in 15 ml toluene}) & (\text{in 2 ml methanol}) \\
1 \text{ mmol DMP} & \quad 1 \text{ mmol KOH} \\
& (\text{in 3 ml toluene}) & (\text{in 2 ml methanol}) \\
\end{align*}
\]

\[\xrightarrow{O_2 \text{ slow addition}}\]

\[\text{products} \]

\[\xrightarrow{\text{precipitating in acidic methanol}}\]

\[\xrightarrow{\text{re-precipitating twice in acidic methanol from CHCl}_3}\]

\[\xrightarrow{\text{drying in vacuo}}\]

\[\text{Scheme 2 Schematic representation of preparation of PPO-20H.}\]

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volume, 30 ml; addition rate of DMP/toluene solution, 0.16 ml/min; T=20 °C; \(P_\text{O}_2\)=101.3 kPa.

6.2.5 Determination of DPQ

After stopping the reaction (the total reaction time is mentioned in Table 1), 1 ml of the reaction mixture was immediately diluted with chloroform and subsequently the concentration of DPQ was determined with a PYE Unicam SP-8-200 UV/VIS Spectrophotometer at 421 nm (\(c=74,000 \text{ dm}^3\cdot\text{mol}^{-1}\cdot\text{cm}^{-1}\)). From these data the percentage of reacted DMP that has been transformed into DPQ was calculated.

6.3 Results and Discussion

A possible mechanism for the copolymerization of DMP with TMBPA is briefly outlined in Scheme 3 (A). This is derived from the proposed mechanism of oxidative coupling polymerization of DMP in the absence of TMBPA [12,14].

In previous investigations using Cu(II)-NMIm complexes as catalysts, it was found that the base is the so-called co-catalyst producing phenolate anions from DMP, which appear to be essential for the start of the reaction [8]. So, one may expect that formation of phenolate anions by base is also the preliminary step in the copolymerization of DMP with TMBPA.

For the copolymerization of DMP with TMBPA under standard conditions, a large excess of TMBPA to Cu(II) ions, e.g. TMBPA/Cu=7.5, results in PPO-2OH with a very broad molecular weight distribution, i.e. a polydispersity index \(D=\frac{\bar{M}_\text{w}}{\bar{M}_\text{n}}\approx 4-8\), owing to the propagation of PPO chains starting from different TMBPA's. On the other hand, a ratio of TMBPA/Cu=0.5, i.e. the ratio of TMBPA-hydroxyl groups to Cu(II) ions equals 1, leads to PPO-2OH with \(D=2.25\). In this case, one may assume that one TMBPA molecule can coordinate with two copper ions and PPO chains grow from both hydroxyl groups of each TMBPA molecule. Obviously, both extremes appear unfavourable for the formation of PPO-2OH with a narrow molecular weight distribution. Therefore, a small excess of TMBPA with respect to Cu(II) ions, i.e. TMBPA/Cu=1, was preferred for further experiments. Table 1 summarizes the results obtained for TMBPA/Cu=1 under standard conditions.

As shown in Scheme 3 (A) a side-on coordinated phenoxyonium cation, as described by Uechi et al. for a p-benzoquinone copper complex [15], can competitively react either with a TMBPA molecule forming PPO-2OH, or with a DMP molecule yielding PPO and DPQ (Scheme 1), depending on which one (TMBPA or DMP) would be attached to the copper ion. In general, TMBPA is expected to
PhO$^-$ or DMP

Scheme 3 (A) Reaction scheme in case of starting the reaction by adding initial base to DMP.

coordinate stronger with copper ion because of its somewhat stronger basicity than DMP. Therefore, the reaction of the DMP phenoxonium cation with TMBPA should be preferred and the main product of this copolymerization would be PPO-2OH.

Addition of all DMP at the beginning of the reaction does not affect the polydispersity index of obtained PPO-2OH, but only results in more DPQ (1.7%) as expected (exp. 5 in Table 1). The corresponding PPO homopolymer can barely be detected in the $^1$H-NMR spectrum of the telechelics (methanol-insoluble fraction) at $\delta=7.1$ ppm (signal f in Fig. 1: three aromatic protons in one PPO end group) [6].

By reducing the initial DMP concentration upon slow addition of DMP during the experiment, the amount of DPQ in the total product becomes only 0.5-0.6% (exp. 1-4 in Table 1). Furthermore, one can no longer detect any PPO formation from the $^1$H-NMR spectra (no signal at $\delta=7.1$ ppm). A typical 300 MHz $^1$H-NMR spectrum of PPO-2OH (Sample 4 in Table 1) is shown in Fig. 2. The assignments are printed on the figure.
Table 1 Copolymerizations of DMP with TMBPA under standard conditions

<table>
<thead>
<tr>
<th>exp. No.</th>
<th>DMP addition time of DMP (min)</th>
<th>TMBPA</th>
<th>additional reaction time (min)</th>
<th>telechelics yield (%) a)</th>
<th>(\bar{M}_n) (GPC)</th>
<th>D</th>
<th>(\bar{M}_n) (NMR) b) (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>5</td>
<td>40</td>
<td>20</td>
<td>25</td>
<td>3950</td>
<td>1.41</td>
<td>3600</td>
</tr>
<tr>
<td>2</td>
<td>10</td>
<td>40</td>
<td>20</td>
<td>43</td>
<td>3600</td>
<td>1.66</td>
<td>3400</td>
</tr>
<tr>
<td>3</td>
<td>20</td>
<td>40</td>
<td>20</td>
<td>77</td>
<td>3750</td>
<td>1.56</td>
<td>4100</td>
</tr>
<tr>
<td>4</td>
<td>10</td>
<td>40</td>
<td>60</td>
<td>60</td>
<td>4300</td>
<td>1.36</td>
<td>5000</td>
</tr>
<tr>
<td>5</td>
<td>20</td>
<td>60</td>
<td>0 c)</td>
<td>44</td>
<td>4200</td>
<td>1.42</td>
<td>3900</td>
</tr>
</tbody>
</table>

a) Wt.% of telechelics as methanol-insoluble fraction.
b) Calculation method taken from reference [6].
c) adding all DMP at the beginning of the reaction.

Fig. 1 300 MHz \(^1\text{H-NMR}\) spectrum of telechelics (sample 5 in Table 1); above is a expansion of the aromatic region of this spectrum, (in CDCl₃).
In addition, Fig. 1 and 2 show no signal at δ=6.87 ppm, which would be expected for TMBPA segments remaining at the ends of PPO-20H chains, i.e. in case of a=0 in Scheme 1 [5-7]. On the contrary, the signal e at δ=6.97 ppm in Fig. 1 and 2 corresponds to TMBPA segments within the PPO-20H chains [5-7]. So, by the present procedure only PPO-20H are obtained that has grown starting from both sides of TMBPA units.

The yields of telechelics in Table 1 are the weight percentages obtained as methanol-insoluble fraction and increase with increasing total amount of added DMP (exp. 1-3 in Table 1). Addition of more DMP might increase the average molecular weight of total PPO-20H. Therefore, a larger amount of PPO-20H will precipitate in acidic methanol from the reaction solution, resulting in higher yields.

$\bar{M}_n$ values in the range of 3400-5000 g.mol$^{-1}$ and $D=1.36-1.66$ for methanol-insoluble PPO-20H are compiled in Table 1. They were derived from GPC measurements and $^1$H-NMR spectra. By taking a 40 minutes longer additional reaction time (exp. 4 versus exp. 2 in Table 1), the yield increases from 43% to 60% and $\bar{M}_n$ increases from 3600/3400 g.mol$^{-1}$ to 4300/5000 g.mol$^{-1}$ (GPC/NMR). Taking account of the fact that no more dioxygen consumption takes place after
20 minutes additional reaction time, one must assume that some other kind of reaction is taking place at the later stage of the copolymerization in exp.4. This is most likely the so-called "re-distribution" between two PPO-2OH chains through a quinone ketal intermediate as proposed by Cooper et al. [16] and Mijs et al. [17], yielding more PPO-2OH with higher $M_n$, which precipitate in an acidic methanol medium after the reaction. Fig.3 shows the GPC traces of these PPO-2OH obtained after shorter and longer additional reaction time (curve A: sample 2 and curve B: sample 4 in Table 1, respectively). The tail in curve A, representing a rather small amount of telechelics with low $M_n$, disappears when taking longer additional reaction time (curve B). Therefore, a smaller D value of 1.36 was observed for sample 4 in Table 1.

![Fig.3 GPC traces of telechelics: (A) sample 2 in Table 1; and (B) sample 4 in Table 1.](image)

In additional small-scale control experiments ([CuCl$_2$] = [KOH] = 3.32 mmol dm$^{-3}$; NMIm/Cu=30; TMBPA/Cu=1; DMP/TMBPA=10; procedures taken as described previously for the oxidative coupling of DMP in a cylindrical reaction vessel with shaking [8,9]), a 40% higher reaction rate was observed by adding initial base to TMBPA instead of to DMP. This implies that once the TMBPA molecule is transformed into its phenolate anion, this TMBPA phenolate anion (TMBPA$^-$) appears to be a stronger coordinating ligand for the bridge between two copper ions [12]. Furthermore, due to the electro-donating isopropylidene group it
can be more readily oxidized to TMBPA phenoxonium cation (TMBPA\(^+\)). In this case, a partial positive charge may remain on one oxygen atom at the head position of TMBPA \([81]\) and this may attack the para position of a DMP molecule through electrophilic substitution, yielding finally PPO-2OH. Such a pathway is outlined in Scheme 3 (B). Obviously, if the growth of PPO chains only starts from the head-oxygen position as mentioned above, DPQ should not be formed. However, 1.4\% of DPQ was still found in the control experiment by adding the initial base to TMBPA and all DMP at the beginning of the reaction (like in exp.5 in Table 1). Therefore, in this case pathway (A) in Scheme 3 seems still to be responsible for the formation of small amounts of DPQ or PPO and some PPO-2OH, probably through a preliminary exchange reaction of TMBPA\(^-\) with the excess DMP yielding some DMP\(^-\), due to stronger acidity of DMP than TMBPA.

![Chemical Reaction Diagram]

Scheme 3 (B) Reaction scheme in case of starting the reaction by adding initial base to TMBPA.

Accordingly, a combination of pathways seems to apply to this copolymerization: during the first oxidation cycle through pathway (A) in Scheme 3, then followed by pathway (B) in Scheme 3.

Finally, attempts to copolymerize DMP with 4,4'—sulfonyldiphenol (I) or
4-phenylazophenol (II) have been undertaken (procedures taken as in Scheme 2).

\[
\text{HO-} \begin{array}{c}
\text{O} \\
\text{S} \\
\text{O} \\
\text{OH}
\end{array} \quad \begin{array}{c}
\text{O} \\
\text{N=N} \begin{array}{c}
\text{O} \\
\text{O}
\end{array}
\end{array}
\]

(I) (II)

Instead of copolymers only the DMP homopolymerization product PPO was obtained with a very low yield (less than 10%). This was confirmed by the $^1$H-NMR spectra of products obtained as methanol-insoluble fractions. It is conceivable that the presence of the electro attracting sulfonyl or azo group in (I) or (II) prevents copolymerization because of the stronger acidity and higher oxidation potential of (I) and (II) with respect to DMP.

6.4 References

(11) Chen, W.; Boven, G. and Challa, G.; Macromolecules, accepted.