Studies on Immobilized polymer-bound imidazole copper(II) complexes as catalysts
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Chapter 3

Oxidative Coupling Polymerization of 2,6-Dimethylphenol Catalyzed by Copper(II) Complexes of Poly(styrene-co-N-vinylimidazole)

Abstract: The oxidative coupling polymerization of 2,6-dimethylphenol (DMP) catalyzed by copper(II) complexes of poly(styrene-co-N-vinylimidazole) (Cu(II)-PS-Im) in toluene/iso-propanol (13/2 v/v) was investigated. The EPR spectra of these complexes indicate that the complex had a mononuclear structure Cu(PS-Im)$_{4}^{2+}$ in solution for higher ligand/copper ratios. This mononuclear complex was found to be a better catalyst precursor for the reaction and more favourable for poly(2,6-dimethyl-1,4-phenylene oxide) (PPO) formation than dinuclear complexes. Viscometric experiments on solutions of polymeric ligands with and without copper(II) ions showed that the decreasing reaction rate for higher ligand/copper ratios may be due to too high concentrations of polymeric ligand, resulting in overlap of polymer coils. The effect of chain loading $\alpha$ with imidazole ligands on the catalytic activity showed an optimum value for $\alpha=0.11$, which was explained predominantly in terms of strain in polymer chain segments between neighbouring ligand groups in the same copper complex. Michaelis-Menten kinetics was observed for the reaction under standard conditions with $k_{2}=0.15$ s$^{-1}$ and $K_{m}^{-1}=0.45$ dm$^{3}$.mol$^{-1}$. The smaller $K_{m}^{-1}$ for Cu(II)-PS-Im than for low molar mass copper(II) complexes of N-methylimidazole (Cu(II)-NMIm) probably originates from steric hindrance of polymer backbone and difficult substitution of polydentate ligands by substrate. The transition of reaction rates to second order in initial copper concentration indicates that dimerization of copper complexes is necessary for re-oxidation of Cu(I) to Cu(II). Methanol as cosolvent appears to be more favourable for a higher $K_{m}^{-1}$ value than iso-propanol in case of Cu(II)-PS-Im as well as Cu(II)-NMIm.

3.1 Introduction

The oxidative coupling polymerization of DMP (Scheme 1) catalyzed by copper(II) complexes of immobilized polymer-bound pyridine or 4-dimethylaminopyridine (DMAP) has been extensively studied in this laboratory [1-3]. In view of the lower intrinsic activity and specificity of the pyridine-based catalysts [4] and too strong a basicity of the DMAP ligands [3], these catalysts were not suitable for continuous processes. On the other hand, copper(II) complexes of $N$-substituted imidazole ligands with mild
basicity [5] possess higher intrinsic activity than complexes with pyridine [6,7]. Therefore, immobilized polymer-bound imidazole copper(II) complexes were expected to be more promising catalysts for the applied reaction.

\[
\text{m} \text{DMP} + \frac{1}{2} \text{m} \text{O}_2 \xrightarrow{\text{catalyst}} \text{PPO} + \frac{1}{2} \text{m} \text{H}_2\text{O}
\]

**Scheme 1**

Recently, we investigated Cu(II)-NMIm as catalyst for the oxidative coupling polymerization of DMP in toluene/iso-propanol (13/2 v/v) and in 1,2-dichlorobenzene/methanol (ODCB/MeOH) (13/2 v/v) [8]. It was found that mononuclear complexes as catalyst precursor are favourable for higher activity and better specificity for PPO formation than dinuclear species. Besides, better specificity for PPO formation and much higher molar mass of PPO were obtained in toluene/iso-propanol than in ODCB/MeOH.

In the present paper dealing with Cu(II)-PS-Im as catalysts, a detailed and systematic study is described of the same oxidative coupling polymerization in toluene/iso-propanol (13/2 v/v) and some other solvent mixtures. Differences in the catalytic nature of Cu(II)-PS-Im and Cu(II)-NMIm and the effect of different solvent systems on the reaction rate will be discussed.

### 3.2 Experimental

#### 3.2.1 Materials

CuCl\textsubscript{2}(H\textsubscript{2}O)\textsubscript{2} was obtained analytically pure from Merck. N-vinylimidazole and styrene (Aldrich) were distilled from KOH under a reduced N\textsubscript{2} atmosphere. DMP (Aldrich) was purified by repeated recrystallization from n-hexane. NaOH, iso-propanol and methanol (Uvasol quality) (Merck) were used without further purification. Toluene (dried over Na) and ODCB (distilled under reduced N\textsubscript{2}
pressure from CaH₂) were also from Merck.

3.2.2 Synthesis and characterization of PS-Im

Radical copolymerization of N-vinylimidazole with styrene was performed in toluene using AIBN as an initiator as described previously [9]. The \( M_n \) values of copolymer samples were determined with a Knauer Membrane Osmometer in chloroform. The chain loading \( \alpha \) of copolymers with imidazole ligands was determined by elemental analysis. All results on synthesis and characterization are compiled in Table 1. In order to obtain copolymers with reliable and narrow ranges of \( \alpha \) values, the final conversions of copolymerizations were taken below 15% instead of the conversions above 40% used before [10]. According to the Fineman and Ross method, the reactivity ratios of the monomers were calculated to be \( r_1 = 0.07 \) and \( r_2 = 7 \) for N-vinylimidazole and styrene, respectively. These values are similar to the values \( r_1 = 0.1 \) and \( r_2 = 10 \) given by Petrak [9] \( (r_2/r_1 = 100 \text{ in both cases}) \).

<table>
<thead>
<tr>
<th>Mole fraction of N-vinylimidazole</th>
<th>Conversion of co-polymerization (%)</th>
<th>( \alpha )</th>
<th>( M_n ) of co-polymers</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.15</td>
<td>13.9</td>
<td>0.03</td>
<td>44 300</td>
</tr>
<tr>
<td>0.31</td>
<td>14.8</td>
<td>0.05</td>
<td>31 000</td>
</tr>
<tr>
<td>0.34</td>
<td>15.0</td>
<td>0.07</td>
<td>43 000</td>
</tr>
<tr>
<td>0.52</td>
<td>12.3</td>
<td>0.11</td>
<td>46 000</td>
</tr>
<tr>
<td>0.62</td>
<td>13.4</td>
<td>0.17</td>
<td>-</td>
</tr>
<tr>
<td>0.66</td>
<td>8.78</td>
<td>0.21</td>
<td>-</td>
</tr>
<tr>
<td>0.71</td>
<td>9.34</td>
<td>0.23</td>
<td>34 000</td>
</tr>
<tr>
<td>0.81</td>
<td>12.0</td>
<td>0.35</td>
<td>-</td>
</tr>
</tbody>
</table>

*Table 1. Data on synthesis and characterization of styrene-N-vinylimidazole copolymers with varying chain loading \( \alpha \)*

\( \alpha \) Copolymerizations were carried out under \( N_2 \) at 60°C for 5 hours; amount of AIBN based on total of monomers is 0.78 mole%; toluene/monomers = 1/1 (v/v).

3.2.3 EPR spectroscopy

The EPR spectra of frozen solutions of Cu(II)-PS-Im complexes in toluene/iso-propanol (13/2 v/v) were recorded on a Varian E-3 (X-band) Spectrometer at -196°C. The same standard conditions as for oxidative coupling polymerization were applied except that no DMP was added to the system.
3.2.4 Oxidative coupling polymerization

The standard conditions for oxidative coupling were: T = 25°C; P_{O_2} = 101.3 kPa; [DMP] = 0.06 mol dm^{-3}; [Cu^{2+}] = [OH^-] = 0.25x[imidazole] = 3.32 mmol dm^{-3}; solvent mixture, toluene/iso-propanol (13/2 v/v); total reaction volume, 0.015 dm^3. Polymeric catalysts were prepared in situ by dissolving the copolymeric ligands in toluene and adding CuCl_2/iso-propanol solution. Hydroxide was added as NaOH in iso-propanol. After saturating the reaction system with O_2, the reactions were started by mixing the catalyst solution with a solution of DMP in toluene. Steady state reaction rates R were calculated by measuring O_2 uptake as a function of time with an automatic isobaric gas burette. The shaking speed of the reaction vessel was high enough to prevent gas-liquid diffusion of O_2 becoming rate determining.

3.2.5 Determination of overall catalytic specificity

Once the reaction was complete, the reaction mixture was diluted with chloroform and the concentration of 3,5,3',5'-tetramethyl-4,4'-diphenoquinone (DPQ) was quickly determined with a PYE Unicam SP-8-200 UV/VIS Spectrophotometer at 421 nm (ε=74,000 dm^3 mol^-1 cm^-1). The percentage of reacted DMP that had been transformed into DPQ could be calculated because PPO and DPQ are practically the sole products.

3.3 Results and Discussion

3.3.1 Structures of Cu(II)-PS-Im in solution

UV spectra failed to give valuable information and EPR spectra seem to be more suitable to indicate the complex structures [8].

The EPR spectrum of a frozen solution of CuCl_2 in toluene/iso-propanol (13/2 v/v) shows the presence of CuCl_2(iso-propanol)_x species (Fig.1 (i): g_L=2.08, g_=2.37, A_=130 Gauss). The addition of polymeric ligands with α=0.11 leads to complete disappearance of CuCl_2(iso-propanol)_x. Obviously, CuCl_2(iso-propanol)_x is converted into some other species, one of them probably being the coordinatively unsaturated, EPR-detectable, mononuclear Cu(PS-Im)_{1-3}^{2+} complex (Fig.1 (ii)-(iv), species a, g_L=2.03, g_=2.24, A_=140 gauss). On further increase of the ligand/copper ratio, the EPR signal of Cu(PS-Im)_{1-3}^{2+} gradually decreases and disappears at ligand/copper=4 (Fig.1 (v)). At the same time, another, EPR-detectable, mononuclear Cu(PS-Im)_4^{2+} complex is observed with very clear superhyperfine splitting [11] (Fig.1 (iii)-(vi), species b, g_L=2.03, g_=2.24, A_=180 Gauss and A_N=15 Gauss).
Fig. 1 EPR spectra of Cu(II)-PS-Im complexes for PS-Im with α=0.11 ([Cu(II)]=3.32 mmol dm$^{-3}$):

(i) ligand/Cu=0, OH/Cu=0, receiver gain (RG)=2x10$^4$;
(ii) ligand/Cu=1, OH/Cu=1, RG=6.2x10$^4$;
(iii) ligand/Cu=2, OH/Cu=1, RG=4x10$^4$;
(iv) ligand/Cu=3, OH/Cu=1, RG=4x10$^4$;
(v) ligand/Cu=4, OH/Cu=1, RG=3.2x10$^4$;
(vi) ligand/Cu=10, OH/Cu=1, RG=2.5x10$^4$.

Although the EPR spectra of the complexes are not integrated, it is clear that variation of the ligand/copper ratio from 1 to 10 gives rise to a gradual enhancement of the total mononuclear complex concentration (Fig. 1 (ii)-(vi); note the decreasing receiver gain values). The EPR signals of the complexes become very broad and show very low intensity for ligand/copper>20, probably due to the overlap of the polymer ligand coils in the solution (see later). On the other hand, the rather weak EPR signals of mononuclear complexes at low
ligand/copper ratios imply that some other, EPR-silent, species must also be present in the solution, probably a dinuclear complex \([8,12]\). Indeed, such dinuclear complexes should be gradually converted into mononuclear ones with increasing ligand/copper ratio and this transformation seems to be almost complete for ligand/copper ratio around 10 (Scheme 2 gives the overall picture).

\[
\begin{align*}
\text{CuCl}_2(\text{iso-propanol})_x & \quad (x=2-6) \\
\downarrow & \text{ligand/Cu}\geq1, \text{OH/Cu=1} \\
\text{Cu(PS-Im)}_{1-3}^{2+} & \leftrightarrow \text{Dimer} \\
\downarrow & \text{ligand/Cu}\geq2 \\
\text{Cu(PS-Im)}_4^{2+} & \leftrightarrow \text{Cu(PS-Im)}_{1-3}^{2+} \leftrightarrow \text{Dimer} \\
\downarrow & \text{ligand/Cu}\geq4 \\
\text{Cu(PS-Im)}_4^{2+} & \leftrightarrow \text{Dimer} \\
\downarrow & \text{ligand/Cu}\geq10 \\
\text{Cu(PS-Im)}_4^{2+} & \downarrow \text{ligand/Cu}\geq20 \\
\text{EPR signal becoming broad} \\
\end{align*}
\]

Dimer:

\[
\begin{align*}
(\text{PS-Im})_{\text{OH}} & \quad \text{Cu} & \quad (\text{PS-Im})_{\text{OH}} \\
(\text{PS-Im})_{\text{OH}} & \quad \text{Cu} & \quad (\text{PS-Im})_{\text{OH}} \\
\end{align*}
\]

**Scheme 2**

### 3.3.2 The role of hydroxide

The reaction rates under standard conditions are plotted as a function of the OH/Cu ratio in Fig.2. With PS-Im ligands no reaction takes place in the absence of base. When the base is added to the DMP solution instead of to the Cu(II)-PS-Im solution, much higher reaction rates and shorter induction periods \((\Delta t)\) are observed. Such effects were also found for Cu(II)-NMIm system \([8]\) and prove that dehydronation of DMP by hydroxide is essential for coordination to Cu(II)-PS-Im complexes. In both cases a maximum in reaction rate is observed, viz. at OH/Cu=2.0 and 1.5, respectively (Fig.2). This indicates that increasing the hydroxide concentration promotes formation of
phenolate anions, resulting in an enhanced reaction rate, whereas an excess of hydroxide somehow destroys the catalyst, causing a decrease in rate. Addition of hydroxide to DMP solution shortens the contact time of copper complex with base and therefore suppresses catalyst destruction, so that higher reaction rates are observed.

\[ R \times 10^6 \quad (\text{mol}\cdot\text{dm}^{-3}\cdot\text{s}^{-1}) \]

![Graph](image)

**Fig. 2** Steady state reaction rate as a function of OH/Cu ratio under standard conditions for PS-Im with \( \alpha = 0.11 \): (Δ) adding base to Cu(II)-PS-Im solution; (o) adding base to DMP solution.

The induction period \( \Delta t = (X) \) min is given in parentheses.

In case of adding base to Cu(II)-NMIm solution, the optimum catalytic activity was found at OH/Cu=1 [8] instead of 2 in the present case. This shift of maximum reaction rate indicates that the stability of complexes against base is improved by introduction of polymeric ligands.

3.3.3 Effect of ligand/copper ratio

As shown in Fig. 3, the optimum reaction rate under standard conditions is
obtained for ligand/copper ratios around 10. In view of the spectroscopic results, it is clear that a higher ligand concentration promotes formation of mononuclear complexes, especially Cu(PS-Im)$_4^{2+}$, which seems to be a good catalyst precursor in the applied system. In the solvent mixture ODCB/MeOH (13/2 v/v) and for ligand/copper<6, Verlaan et al. [6] also found increasing reaction rates for higher ligand/copper ratios.

![Figure 3](image)

**Fig. 3** Steady state reaction rate as a function of ligand/Cu ratio under standard conditions for PS-Im with:

- (o) $\alpha=0.07$
- (A) $\alpha=0.11$
- (o) $\alpha=0.23$

By performing some viscometric experiments on solutions of polymeric ligands with and without copper ions, it is observed that the specific viscosities ($\eta_{sp}$) of the solutions give a stronger increase above polymer concentrations of 0.06 g.ml$^{-1}$, which corresponds to ligand/copper=12 (Fig.4). Therefore, it is assumed that the decrease in reaction rate in Fig.3 for ligand/copper>10 is caused at least part by overlap of the polymer ligand coils. Of course, this situation is different from that for Cu(II)-NMIm, in
which case increasing reaction rates were still observed for ligand/copper $> 20$ [8].

![Fig.4 Plot of log $(\eta^\text{sp})$ versus log C (C is the concentration in g.ml$^{-1}$) for solutions of Cu(II)-PS-Im with $\alpha=0.07$ under standard conditions: (A) in toluene/iso-propanol (13/2 v/v); (o) in toluene/MeOH (13/2 v/v) (ligand/Cu values are indicated at the top of the Figure); (o) for solutions of PS-Im with $\alpha=0.03$ in the absence of copper ions in toluene/iso-propanol (13/2 v/v).

The specificity of the oxidative coupling polymerization of DMP catalyzed by Cu(II)-PS-Im complexes was studied in toluene/iso-propanol (13/2 v/v). Enhanced PPO formation is obtained with increasing ligand/copper ratio, as shown in Fig.5 for $\alpha=0.07$, 0.11 and 0.23. A DPQ yield of only 5% is found for ligand/copper=10. So, the good specificity in case of Cu(II)-NMIm [8] is also observed for Cu(II)-PS-Im. Considering the spectroscopic results, it seems
obvious that the mononuclear Cu(II)-PS-Im complex with four ligands as catalyst precursor is more favourable for C-O coupling leading to PPO formation than dinuclear species (see Scheme 2).

![Fig.5](image)

**Fig.5** Effect of ligand/Cu ratio on final specificity under standard conditions for PS-Im with:
(a) $\alpha=0.07$;  (A) $\alpha=0.11$;  (o) $\alpha=0.23$.

3.3.4 Effect of chain loading $\alpha$

Fig.5 also shows that the specificity of Cu(II)-PS-Im is unaffected by the degree of loading $\alpha$ of the copolymers with imidazole ligands. This implies that the macromolecular chain itself does not influence the catalytic specificity, which was also observed in previous investigations with pyridine or DMAP-type ligands [4,13].

However, the effect of chain loading $\alpha$ on the reaction rate is pronounced, as shown in Fig.6 under standard conditions with ligand/copper=4 and 10. For both ratios a maximum in the reaction rate is found around $\alpha=0.11$. This is in accordance with EPR spectroscopic results, which show that an
increase in $\alpha$ value up to $\alpha=0.11$ gives an enhanced amount of $\text{Cu(PS-Im)}_{4}^{2+}$ and a decline of $\text{Cu(PS-Im)}_{4-3}^{2+}$ species. However, this is not appropriate to describe the maximum in the effect of $\alpha$ on the reaction rate. As reported by Schouten and Challa [14,15], strain in the polymer chain segments between neighbouring ligand groups may also play an important role in the effect of $\alpha$ on the activity of the catalyst. For copper(II) complexes of polymer-bound dimethylamine and pyridine, it was shown by Challa et al. [7,16] that the increase of the electron-transfer rate with increasing $\alpha$ is governed by an enhancement of the activation entropy ($\Delta S^\ddagger$), which overcompensates for the retarding effect of a simultaneously increasing activation enthalpy ($\Delta H^\ddagger$). This explanation was supported by statistical calculations of intermediate chain conformations and by measurement of the heat of complexation of copper(II) ions with polymeric ligands for varying $\alpha$.

![Figure 6](image)

**Fig.6** Steady state reaction rate as a function of chain loading $\alpha$ with imidazole ligands under standard conditions:

(A) ligand/Cu=4; (o) ligand/Cu=10.
It seems plausible that the above-mentioned explanation is also valid for the observed effect of $\alpha$ on the reaction rate in the present system. So, with increasing $\alpha$ the intermediate chain between neighbouring imidazole ligands becomes shorter and the strain in the catalyst increases. This causes an enhancement of $\Delta S^\ddagger$ for the electron transfer from substrate to copper(II).

When the intermediate chain between neighbouring imidazole ligands becomes too short, i.e. for $\alpha>0.11$ in the present case, adjacent ligands can not coordinate to the same copper(II) ion any longer. In other words, one or more ligands have to be skipped over in favor of subsequent ones. Consequently, the strain in the polymer catalyst is reduced, resulting in a decreasing reaction rate. In fact, the skipped coordination of ligands to copper ions can be considered as a lowering of the "effective" value of $\alpha$, which leads to lower reaction rate.

On the other hand, ligands skipped for steric reasons can coordinate with copper(II) ions attached to other sites on the same polymer backbone, which can be considered as a kind of intramolecular crosslinking. Besides, the smaller styrene group content of the polymer backbone for higher $\alpha$ may result in a reduced hydrophobicity around active centers. Both effects may reduce the accessibility of catalytically active sites for the substrate, which should have an extra retarding effect on the reaction rate.

### 3.3.5 Kinetics of oxidative coupling

Under standard conditions, reaction rates were measured for different DMP concentrations. So-called saturation kinetics are observed, as shown in Fig. 7 (curve (A)). Therefore, the oxidative coupling polymerization of DMP catalyzed by Cu(II)-PS-Im complexes in toluene/iso-propanol can be described by a Michaelis-Menten mechanism as given in Scheme 3. In this scheme, $E$ is the active copper(II) complex; $E^*$ is the Cu(I) complex; $[E]_0$ = overall concentration of copper salt; $k_2$ = rate constant of rate-determining step; and $K_m = (k_{-1} + k_2)/k_1$ is the Michaelis-Menten constant.

From the double-reciprocal Lineweaver-Burk plot of reaction rate versus DMP concentration obeying the well-known equation:

$$\frac{1}{R} = \frac{1}{k_2[E]_0} + \frac{K_m}{k_2[E]_0[DMP]}$$

$k_2$ and $K_m^{-1}$ (a measure of the accessibility of active site for DMP) have been calculated, yielding $k_2 = 0.15 \, s^{-1}$ and $K_m^{-1} = 0.45 \, dm^3\, mol^{-1}$. Table 2 gives the values of $k_2$ and $K_m^{-1}$ for both Cu(II)-NMIm and Cu(II)-PS-Im in different
Fig. 7 Steady state reaction rate as a function of initial DMP concentration under standard conditions:
(A) adding base to Cu(II)-PS-Im for PS-Im with $\alpha=0.11$; 
(o) adding base to DMP solution for PS-Im with $\alpha=0.07$.

![Diagram showing reaction rates and solvent mixtures. An almost identical rate constant ($k_2$) of the rate-determining step is observed in all cases, which implies that the intrinsic activity of the catalyst depends mainly on the nature of the solvent mixtures.](image)

Scheme 3

solvent mixtures. An almost identical rate constant ($k_2$) of the rate-determining step is observed in all cases, which implies that the intrinsic activity of the catalyst depends mainly on the nature of the
imidazole ligand itself. However, the values of $K_m^{-1}$ are much smaller for 
$\text{Cu(II)}$-$\text{PS-Im}$ than for $\text{Cu(II)}$-$\text{NMIm}$ in all solvent systems. In general, a higher 
local active center concentration in the polymer coils may enhance the $K_m^{-1}$ 
value. On the contrary, steric hindrance of the polymer backbone and more 
difficult substitution of a polydentate ligand by substrate will have negative 
effects. In the present case of $\text{Cu(II)}$-$\text{PS-Im}$ as catalyst, it seems that latter 
effects predominate and hamper the substitution of a polymeric ligand by 
substrate. The effect of solvent mixture on $K_m^{-1}$ will be discussed later.

Notably, saturation kinetics in DMP was also found when adding the base 
to DMP solution, yielding phenolate anions (Fig. 7, curve (c)), although the 
reaction rates were higher (see also Fig. 2). This indicates that a phenolate 
anion-containing copper(II) complex is coordinated by a DMP molecule before 
the rate-determining step takes place.

### 3.3.6 Reaction order in $[\text{Cu(II)}]$ 

In the studies of polymer-bound DMAP copper(II) complexes as catalyst for 
the oxidative coupling polymerization of DMP, Koning et al. [17] suggested 
that dimerization of mononuclear copper complexes is necessary for the 
re-oxidation of Cu(I) to Cu(II). For constant amounts of polymeric ligands 
with $\alpha=0.17$ and 0.05 ([imidazole]= 26.4 and 13.2 mmol.dm$^{-3}$, respectively),

<table>
<thead>
<tr>
<th>Complex</th>
<th>Solvent system</th>
<th>Ligand/Cu</th>
<th>$k_2^{-1}$ (s$^{-1}$)</th>
<th>$K_m^{-1}$ (dm$^3$.mol$^{-1}$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>$\text{Cu(II)}$-$\text{NMIm}$</td>
<td>toluene/iso-propanol</td>
<td>30</td>
<td>0.15</td>
<td>9.1</td>
</tr>
<tr>
<td>$\text{Cu(II)}$-$\text{NMIm}$</td>
<td>toluene/MeOH</td>
<td>30</td>
<td>0.15</td>
<td>12.5</td>
</tr>
<tr>
<td>$\text{Cu(II)}$-$\text{PS-Im}$</td>
<td>ODCB/MeOH</td>
<td>30</td>
<td>0.12</td>
<td>12.6</td>
</tr>
<tr>
<td>$\text{Cu(II)}$-$\text{PS-Im}$</td>
<td>toluene/iso-propanol</td>
<td>4</td>
<td>0.11</td>
<td>0.45</td>
</tr>
<tr>
<td>$\text{Cu(II)}$-$\text{PS-Im}$</td>
<td>toluene/MeOH</td>
<td>4</td>
<td>0.17</td>
<td>1.69</td>
</tr>
<tr>
<td>$\text{Cu(II)}$-$\text{PS-Im}$</td>
<td>ODCB/MeOH</td>
<td>2</td>
<td>0.14</td>
<td>1.3 [6]</td>
</tr>
</tbody>
</table>

Fig. 8 shows a first-order rate dependence on $[\text{Cu(II)}]$ for log$[\text{Cu(II)}]>-3.1$ 
([Cu(II)]>0.83 mmol.dm$^{-3}$) and a second-order rate dependence on $[\text{Cu(II)}]$ for 
log$[\text{Cu(II)}]<-3.1$ ([Cu(II)]<0.83 mmol.dm$^{-3}$). This result indicates that, under 
standard conditions with $[\text{Cu(II)}]=3.32$ mmol.dm$^{-3}$, the local dimerization of
copper complexes is so fast that the oxidation rate of DMP ($k_2$) is rate-determining and the overall reaction is first-order in [Cu(II)]. On the contrary, for the low concentrations of copper(II) ions, the dimerization will become rate-determining. Then a second-order rate dependence on [Cu(II)] is observed. In the present case it appears that the transition from first to second order takes place at such [Cu(II)] that on the average only about one copper ion is present per polydentate coil. Consequently, dimerization will also be retarded because it often requires reaction between copper ions complexed in different polydentate coils.

Fig. 8 Plot of log R versus log [Cu(II)] under standard conditions for PS-Im with:

(A) $\alpha=0.17$ and [imidazole]=26.6 mmol.dm$^{-3}$;

(o) $\alpha=0.05$ and [imidazole]=13.3 mmol.dm$^{-3}$.

Ligand/Cu values for $\alpha=0.17$ are indicated at the top of the Figure; the values in parentheses are for $\alpha=0.05$; R is the steady state reaction rate in mol.dm$^{-3}$.s$^{-1}$; [Cu(II)] in mol.dm$^{-3}$. 

\[ \text{Fig. 8 Plot of log } R \text{ versus log } [\text{Cu(II)}] \]
3.3.7 Effect of solvent system on reaction rate

As shown in Fig. 9 the reaction rates with Cu(II)-PS-Im or Cu(II)-NMIm are smaller for toluene/iso-propanol than for toluene/MeOH or ODCB/MeOH in the applied range of ligand/copper ratios. Table 2 also demonstrates that higher $K_m^{-1}$ values are observed in toluene/MeOH or ODCB/MeOH than in toluene/iso-propanol. Obviously, this phenomenon is primarily related to either methanol or iso-propanol being used as cosolvent, rather than to expansion or

Fig. 9 Steady state reaction rate as a function of ligand/Cu ratio under standard conditions in different solvent systems.

For Cu(II)-NMIm: (Δ) toluene/iso-propanol (13/2 v/v);
(a) toluene/MeOH (13/2 v/v);
(o) ODCB/MeOH (13/2 v/v).

For Cu(II)-PS-Im: (Δ) toluene/iso-propanol (13/2 v/v) and α=0.23;
(a) toluene/MeOH (13/2 v/v) and α=0.23;
(o) ODCB/MeOH (13/2 v/v) and α=0.17.
contraction of the polymeric ligands in solution. In fact, the same specific viscosities ($\eta_{sp}$) are observed for solutions of polymeric ligands in either toluene/MeOH or toluene/iso-propanol (see Fig.4). So, coordinated methanol seems to be more accessible to substitution by substrate than iso-propanol.

Fortunately, methanol gives only a slight decrease in catalytic specificity, i.e. under standard conditions with ligand/copper=10 for PS-Im with $\alpha=0.23$, a DPQ yield of 7% is found in toluene/MeOH as compared to 5% in toluene/iso-propanol in Fig.5. Therefore, we prefer to use toluene/MeOH (13/2 v/v) as solvent mixture in future studies on immobilized polymer-bound imidazole copper(II) complexes.

3.4 References