Studies on immobilized polymer-bound imidazole–copper(II) complexes as catalysts: 1. Oxidative coupling polymerization of 2,6-dimethylphenol catalysed by copper(II) complexes of poly(styrene-*co*-*N*-vinylimidazole)

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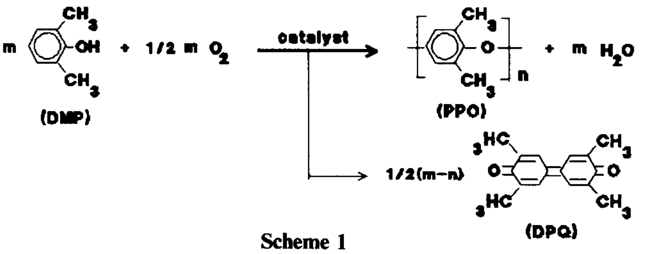
The oxidative coupling polymerization of 2,6-dimethylphenol catalysed by copper(II) complexes of poly(styrene-*co*-*N*-vinylimidazole) (Cu(II)–PS-Im) in toluene/isopropanol (13/2 v/v) was investigated. The electron paramagnetic resonance spectra of these complexes indicate that the complex had a mononuclear structure $\mathrm{Cu(PS\text{-}Im)_4^{2+}}$ in solution for higher ligand/copper ratios. This mononuclear complex was found to be a more active catalyst for the reaction and more favourable for poly(2,6-dimethyl-1,4-phenylene oxide) 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 α 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 were observed for the reaction under standard conditions with $k_2 = 0.15\,\mathrm{s^{-1}}$ and $K_m^{-1} = 0.45\,\mathrm{dm^3\,mol^{-1}}$. 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 to second order in copper indicates that dimerization of mononuclear Cu(I) complexes is necessary for reoxidation of Cu(I) to Cu(II). Methanol as cosolvent appears to be more favourable for a higher K_m^{-1} value than isopropanol in the case of Cu(II)–PS-Im as well as Cu(II)–NMIm.

(Keywords: polystyrene-bound imidazole-copper (II); polymeric catalysts; catalytic activity and specificity; phenol oxidation)

INTRODUCTION

The oxidative coupling polymerization of 2,6-dimethylphenol (DMP) (*Scheme 1*) catalysed by copper(II) complexes of immobilized polymer-bound pyridine or 4-dimethylaminopyridine (DMAP) has been extensively studied in this laboratory[1–3] (Scheme 1). 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 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.



Scheme 1

Recently, we investigated copper(II) complexes of *N*-methylimidazole (Cu(II)–NMIm) as catalysts for the oxidative coupling polymerization of DMP in toluene/isopropanol (13/2 v/v) and in 1,2-dichlorobenzene/methanol (oDCB/MeOH) (13/2 v/v)[8]. It was found that mononuclear complexes are favourable for higher catalytic activity and better specificity for poly(2,6-dimethyl-1,4-phenylene oxide) (PPO) formation than dinuclear species. Besides, better specificity for PPO formation and much higher molar mass of PPO were obtained in toluene/isopropnaol than in oDCB/MeOH.

In the present paper dealing with copper(II) complexes of poly(styrene-*co*-*N*-vinylimidazole) (Cu(II)–PS-Im) as catalysts, a detailed and systematic study is described of the same oxidative coupling reaction in toluene/isopropanol (13/2 v/v) and some other solvent mixtures. Differences in the catalytic nature of Cu(II)–PS-Im and

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Cu(II)–NMIm and the effect of different solvent systems on the reaction rate will be discussed.

EXPERIMENTAL

Materials

$CuCl_2(H_2O)_2$ was obtained analytically pure from Merck. *N*-Vinylimidazole and styrene, both from Aldrich, were distilled from KOH under a reduced N_2 atmosphere. DMP from Aldrich was purified by repeated recrystallization from n-hexane. NaOH, isopropanol and methanol (Uvasol quality) from Merck were used without further purification. Toluene (dried over Na) and oDCB (distilled under reduced N_2 pressure from CaH_2) were also from Merck.

*Synthesis and characterization of poly(styrene-*co*-N-vinylimidazole)*

Radical copolymerization of styrene and *N*-vinylimidazole was performed in toluene using azobisisobutyronitrile (AIBN) as initiator as described previously[9]. The $\bar{M}_n$ values of copolymer samples were determined with a Knauer membrane osmometer in chloroform. The chain loading α of copolymers with imidazole ligand 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 α 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 $r_2 = 7.0$ 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] ($r_2/r_1 = 100$ in both cases).

E.p.r. spectroscopy

The e.p.r. spectra of frozen solutions of Cu(II)–PS-Im complexes in toluene/isopropanol (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.

Oxidative coupling polymerization

The standard conditions for oxidative coupling were: $T = 25°C$; $P_{O_2} = 101.3\,kPa$; $[DMP] = 0.06\,mol\,dm^{-3}$; $[Cu^{2+}] = [OH^-] = 0.25 \times [imidazole] = 3.32 \times 10^{-3}\,mol\,dm^{-3}$; solvent mixture, toluene/isopropanol (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 $CuCl_2$/isopropanol solution. Hydroxide was added as NaOH in isopropanol. 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.

Table 1 Data on synthesis and characterization of styrene-*co*-*N*-vinylimidazole copolymers with varying chain loading α[a]

Mole fraction of *N*-vinylimidazole	Conversion of copolymerization (%)	α	$\bar{M}_n$ of copolymers
0.15	13.9	0.03	44300
0.31	14.8	0.05	31000
0.34	15.0	0.07	43000
0.52	12.3	0.11	46000
0.62	13.4	0.17	–
0.66	8.78	0.21	–
0.71	9.34	0.23	34000
0.81	12.0	0.35	–

[a] Copolymerizations were carried out under N_2 at 60°C for 5 h; amount of AIBN based on total of monomers is 0.78 mol%; toluene/monomers = 1/1 (v/v)

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 u.v./v.i.s. spectrophotometer at 421 nm ($\varepsilon = 74\,000\,dm^3\,mol^{-1}\,cm^{-1}$). The percentage of reacted DMP that has been transformed into DPQ could be calculated because PPO and DPQ are practically the sole products.

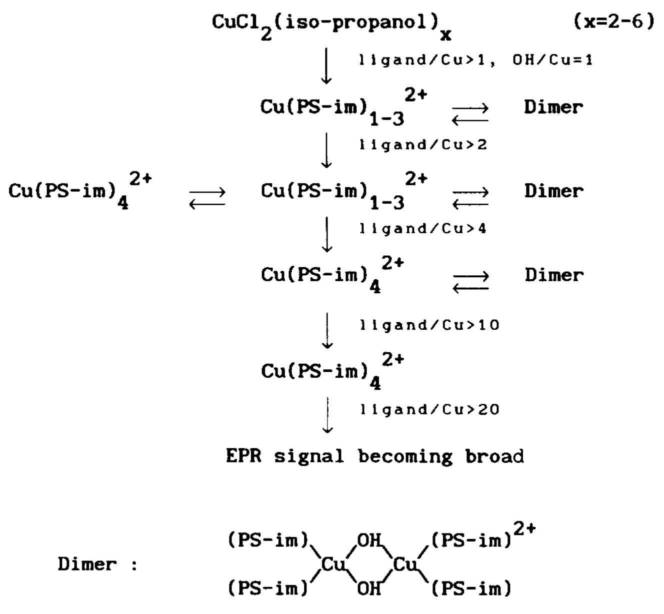
RESULTS AND DISCUSSION

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

U.v. spectra failed to give valuable information and e.p.r. spectra seem to be more suitable to indicate the complex structures[8].

The e.p.r. spectrum of a frozen solution of $CuCl_2$ in toluene/ispropanol (13/2 v/v) shows the presence of $CuCl_2(isopropanol)_x$ species (*Figure 1* (i), $g_\perp = 2.08$, $g_\parallel = 2.37$, $A_\parallel = 130\,G$). The addition of polymeric ligands with $\alpha = 0.11$ leads to complete disappearance of $CuCl_2(isopropanol)_x$. Obviously, $CuCl_2(isopropanol)_x$ is converted into some other species, one of them probably being the coordinatively unsaturated, e.p.r.-detectable, mononuclear $Cu(PS\text{-}Im)_{1-3}^{2+}$ complex (*Figure 1* (ii)–(iv), species a, $g_\perp = 2.03$, $g_\parallel = 2.24$, $A_\parallel = 140\,G$). On further increase of the ligand/copper ratio, the e.p.r. signal of $Cu(PS\text{-}Im)_{1-3}^{2+}$ gradually decreases and disappears at ligand/copper = 4 (*Figure 1* (v)). At the same time, another, e.p.r.-detectable, mononuclear $Cu(PS\text{-}Im)_4^{2+}$ complex is observed with very clear superhyperfine splitting[11] (*Figure 1* (iii)–(iv), species b, $g_\perp = 2.03$, $g_\parallel = 2.24$, $A_\parallel = 180\,G$ and $A_N = 15\,G$).

Although the e.p.r. 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 (*Figure 1* (ii)–(vi); note the decreasing receiver gain values). The e.p.r. 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 e.p.r. signals of mononuclear complexes at low ligand/copper ratios imply that some other, e.p.r.-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).



Scheme 2

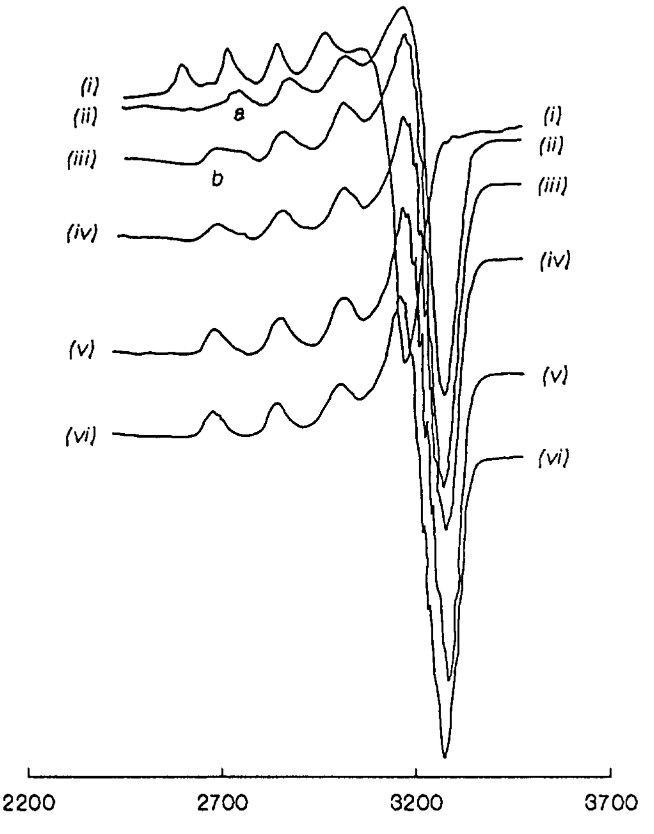


Figure 1 E.p.r. spectra of Cu(II)–PS-Im complexes for PS-Im with $\alpha = 0.11$ ($[CuCl_2] = 3.32 \times 10^{-3}$ mol dm^{-3}): ligand/Cu = 0, OH/Cu = 0, receiver gain (RG) = 2.0×10^4; (ii) ligand/Cu = 1.0, OH/Cu = 1.0, RG = 6.2×10^4; (iii) ligand/Cu = 2.0, OH/Cu = 1.0, RG = 4.0×10^4; (iv) ligand/Cu = 3.0, OH/Cu = 1.0, RG = 4.0×10^4; (v) ligand/Cu = 4.0, OH/Cu = 1.0, RG = 3.2×10^4; (vi) ligand/Cu = 10.0, OH/Cu = 1.0, RG = 2.5×10^4

The role of hydroxide

The reaction rates under standard conditions are plotted as a function of the OH/Cu ratio in *Figure 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 (Δt) are observed. Such effects were also found for the Cu(II)–NMIm system[8] and prove that deprotonation 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 (*Figure 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.

In the case of adding base to Cu(II)–NMIm solution, the optimum catalytic activity was found at OH/Cu = 1.0 (ref. 8) instead of 2.0 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.

Effect of ligand/copper ratio

As shown in *Figure 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 $Cu(PS\text{-}Im)_4^{2+}$, which seems to be the most active catalyst 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.

By performing some viscometric experiments on solutions of polymeric ligands with and without copper ions, it is observed that the specific viscosities (η_{sp}) of the solutions give a stronger increase above polymer concentrations of 0.06 g ml^{-1}, which corresponds to ligand/

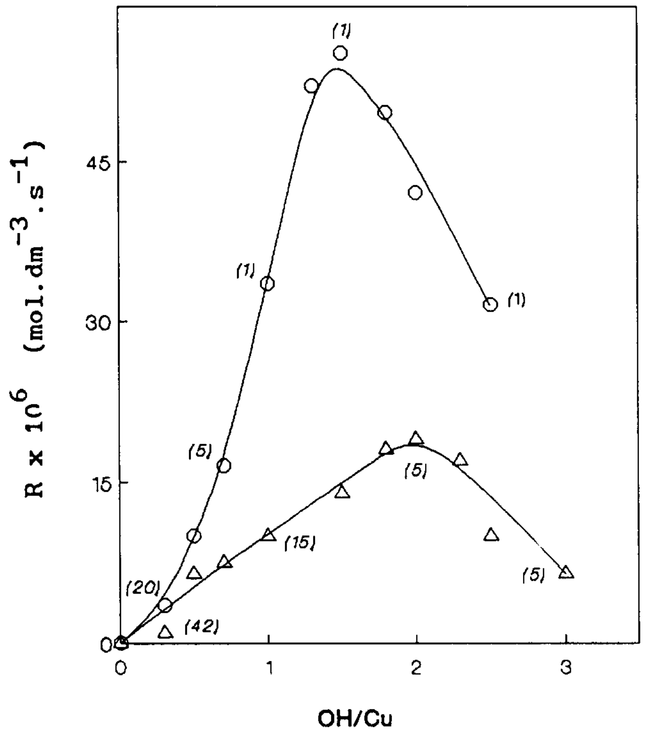


Figure 2 Steady-state reaction rate as a function of OH/Cu ratio under standard conditions for PS-Im with $\alpha = 0.11$: (△) adding base to Cu(II)–PS-Im solution; (○) adding base to DMP solution. The induction period (Δt in minutes) is given in parentheses

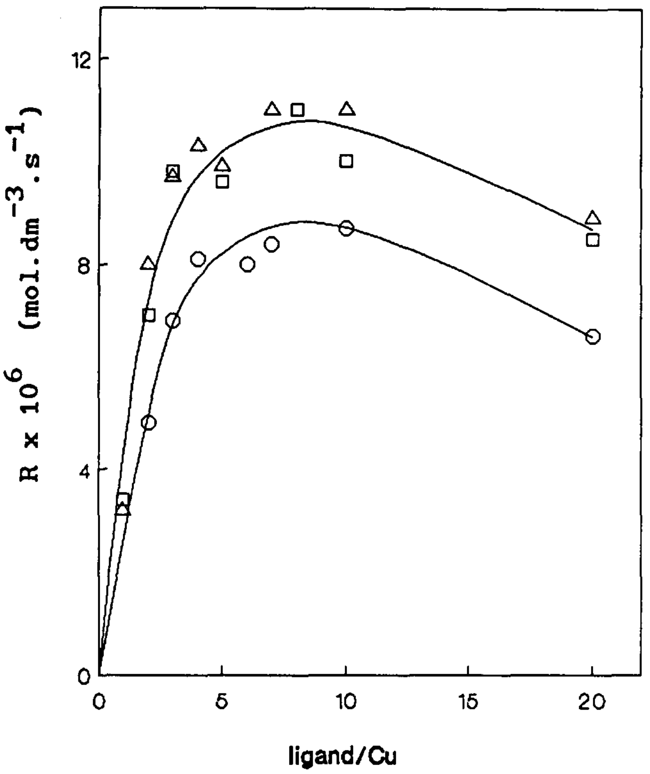


Figure 3 Steady-state reaction rate as a function of ligand/Cu ratio under standard conditions for PS-Im with: (□) $\alpha=0.07$; (△) $\alpha=0.11$; (○) $\alpha=0.23$

copper = 12 (*Figure 4*). Therefore, it is assumed that the decrease in reaction rate in *Figure 3* for ligand/copper > 10 is caused at least partly 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 (ref 8).

The specificity of the oxidative coupling polymerization of DMP catalysed by Cu(II)–PS-Im complexes was studied in toluene/isopropanol (13/2 v/v). Enhanced PPO formation is obtained with increasing ligand/copper ratio, as shown in *Figure 5* for $\alpha=0.07$, 0.11 and 0.23. A DPQ yield of only 5.0% is found for ligand/copper = 10. So, the good specificity in the 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 is more favourable for C–O coupling leading to PPO formation than dinuclear species (see *Scheme 2*).

Effect of chain loading α

Figure 5 also shows that the specificity of Cu(II)–PS-Im is unaffected by the degree of loading α 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 α on the reaction rate is pronounced, as shown in *Figure 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 e.p.r. spectroscopic results, which show that an increase in α value up to $\alpha=0.11$ gives an enhanced amount of the most active Cu(PS-Im)$_4^{2+}$ and a decline of Cu(PS-Im)$_{1-3}^{2+}$ species. However, this is not appropriate to describe the maximum in the

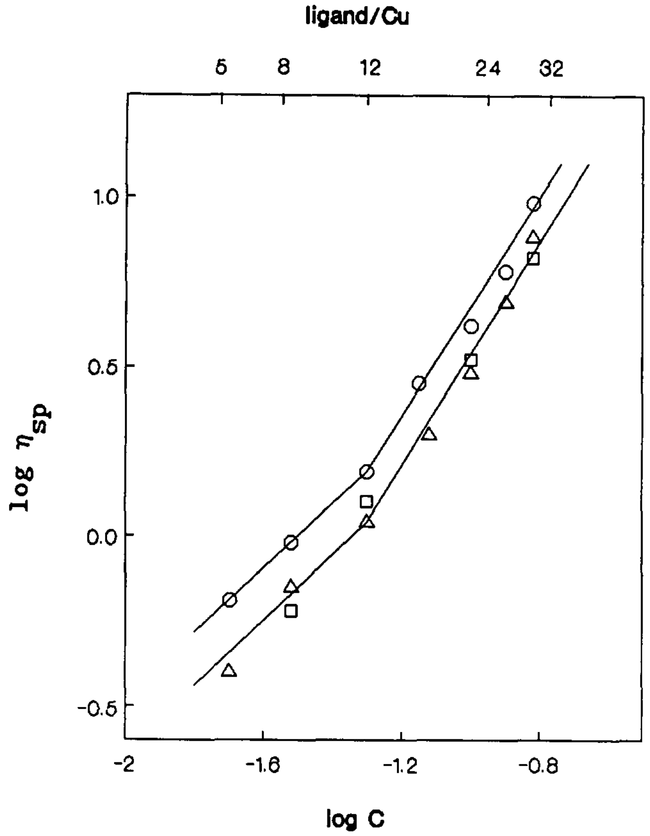


Figure 4 Plot of log(η_{sp}) *versus* log *C* (*C* is the concentration in g ml^{-1}) for solutions of Cu(II)–PS-Im with $\alpha=0.07$ under standard conditions: (△) in toluene/isopropanol (13/2 v/v); (□) in toluene/MeOH (13/2 v/v) (ligand/Cu values are indicated at the top of the figure); (○) for solutions of PS-Im with $\alpha=0.03$ in the absence of copper ions in toluene/isopropanol (13/2 v/v)

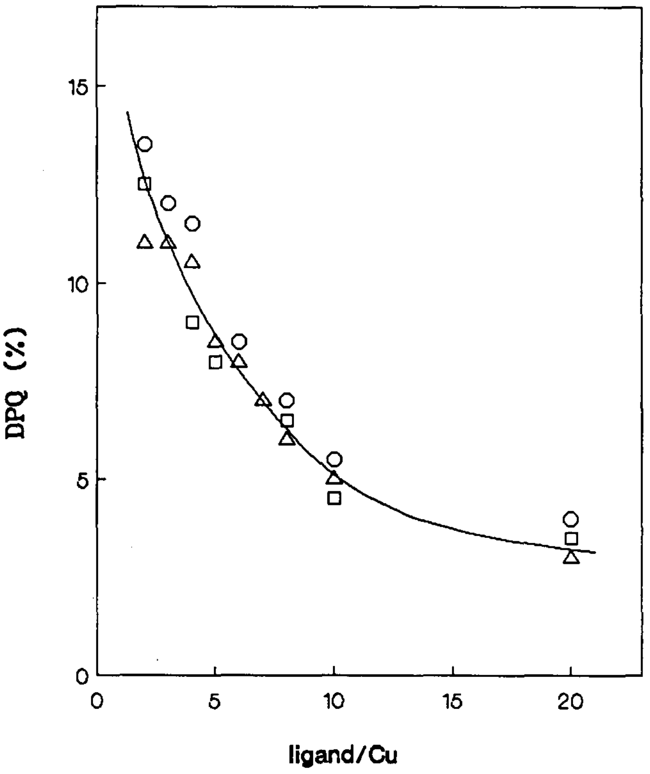


Figure 5 Effect of ligand/Cu ratio on final specificity under standard conditions for PS-Im with: (□) $\alpha=0.07$; (△) $\alpha=0.11$; (○) $\alpha=0.23$

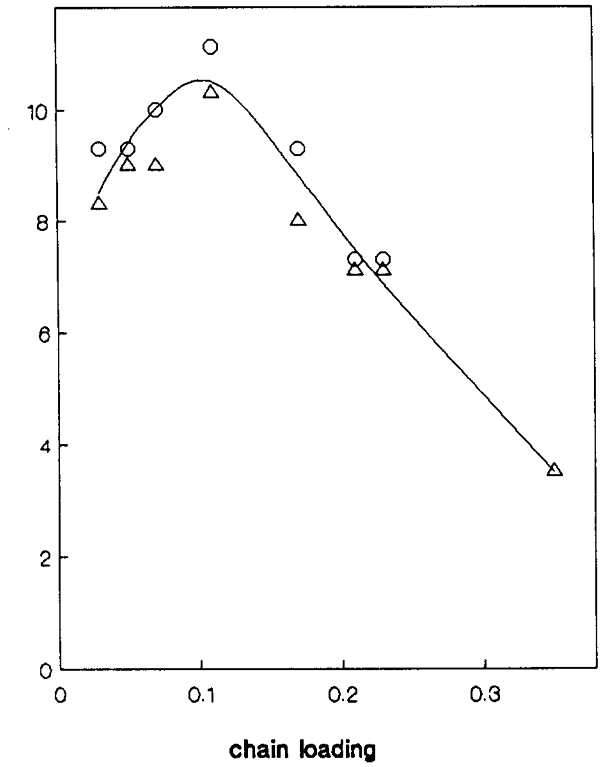


Figure 6 Steady-state reaction rate as a function of chain loading α with imidazole ligands under standard conditions: (△) ligand/Cu = 4; (○) ligand/Cu = 10

effect of α 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 α 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 α 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 α.

It seems plausible that the above-mentioned explanation is also valid for the observed effect of α on the reaction rate in the present system. So, with increasing α 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 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 cannot coordinate to the same copper(II) ion any longer. In other words, one or more ligands have to be skipped over in favour 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 α, which leads to lower reaction rate.

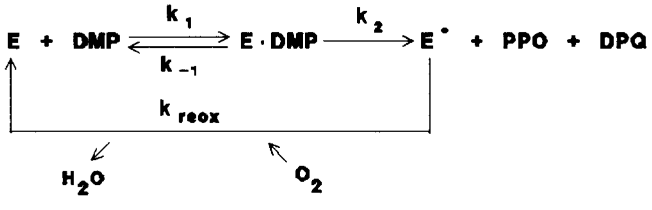
On the other hand, ligands skipped for steric reasons can coordinate with copper(II) ions attached to other sites on the same polymer backbone, which can be considered as a kind of intramolecular crosslinking. Besides, the smaller styrene group content of the polymer backbone for higher α may result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

Kinetics of oxidative coupling

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

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

$$\frac{1}{R}=\frac{1}{k_2[\mathrm{E}]_0}+\frac{K_\mathrm{m}}{k_2[\mathrm{E}]_0[\mathrm{DMP}]}$$



Scheme 3

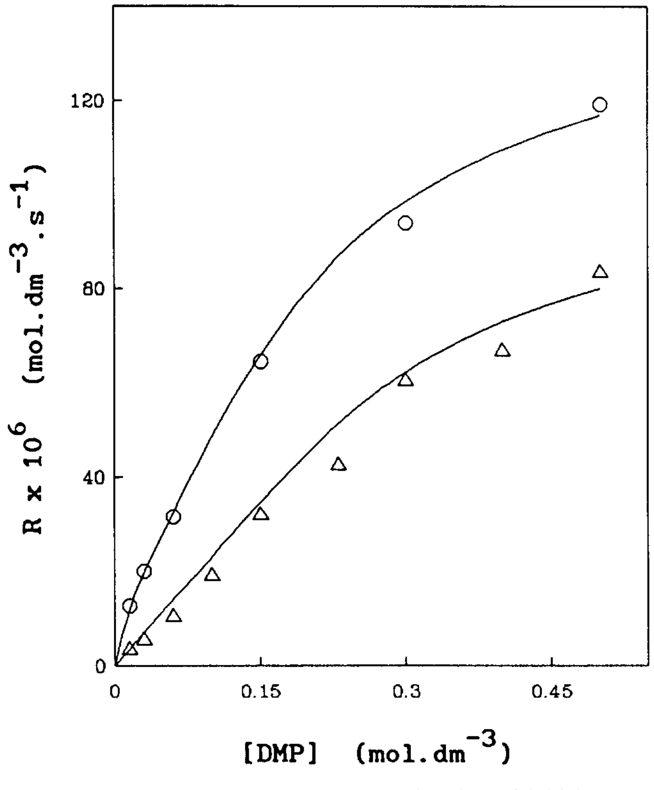


Figure 7 Steady-state reaction rate as a function of initial DMP concentration under standard conditions: (△) adding base to Cu(II)–PS-Im solution for PS-Im with α = 0.11; (○) adding base to DMP solution for PS-Im with α = 0.07

Table 2 Kinetic parameters of oxidative coupling of DMP catalysed by Cu(II)–NMIm and Cu(II)–PS-Im complexes under standard conditions

Complex	Solvent system (13/2 v/v)	Ligand/Cu	α	k_2 (s^{-1})	K_m^{-1} ($dm^3 mol^{-1}$)
Cu(II)–NMIm	Toluene/isopropanol	30	–	0.15	9.10
Cu(II)–NMIm	Toluene/MeOH	30	–	0.15	12.5
Cu(II)–NMIm	oDCB/MeOH	30	–	0.12	12.6
Cu(II)–PS-Im	Toluene/isopropanol	4	0.11	0.15	0.45
Cu(II)–PS-Im	Toluene/MeOH	4	0.17	0.15	1.69
Cu(II)–PS-Im	oDCB/MeOH	2	0.14	0.13	1.30^{6}

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 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 Cu(II)–PS-Im than for Cu(II)–NMIm in all solvent systems. In general, a higher local active centre 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 Cu(II)–PS-Im as catalyst, it seems that latter effects predominate and hamper the substitution of a polymeric ligand by DMP. The effect of solvent mixture on K_m^{-1} will be discussed later.

Notably, saturation kinetics in DMP were also found when adding the base to DMP solution, yielding phenolate anions (*Figure 7* (○ curve)), although the reaction rates were higher (see also *Figure 2*). This indicates that a phenolate anion-containing copper(II) complex is coordinated by a DMP molecule before the rate-determining step takes place. This is in agreement with a mechanism recently proposed by Viersen *et al.*[17].

Reaction order in $[Cu^{2+}]$

In the studies of polymer-bound DMAP–copper(II) complexes as catalysts for the oxidative coupling polymerization of DMP, Koning *et al.*[18] suggested that dimerization of mononuclear Cu(I) complexes is necessary for the reoxidation of Cu(I) to Cu(II). For constant amounts of polymeric ligands with $\alpha = 0.17$ and 0.05 ([imidazole] $= 26.4 \times 10^{-3}$ and $13.2 \times 10^{-3}\,mol\,dm^{-3}$, respectively), *Figure 8* shows a first-order rate dependence on $[Cu^{2+}]$ for $\log[Cu^{2+}] > -3.1$ ($[Cu^{2+}] > 0.83 \times 10^{-3}\,mol\,dm^{-3}$) and a second-order rate dependence on $[Cu^{2+}]$ for $\log[Cu^{2+}] < -3.1$ ($[Cu^{2+}] < 0.83 \times 10^{-3}\,mol\,dm^{-3}$). This result indicates that, under standard conditions with $[Cu^{2+}] = 3.32 \times 10^{-3}\,mol\,dm^{-3}$, the local dimerization of Cu(I) is so fast that the oxidation rate of DMP (k_2) is rate-determining and the overall reaction is first-order in $[Cu^{2+}]$. On the contrary, for the low concentrations of copper(II) ions, the dimerization of Cu(I) complexes followed by the reoxidation of Cu(I) to Cu(II) (k_{reox}) will become rate-determining. Then a second-order rate dependence on $[Cu^{2+}]$ is observed. In the present case it appears that the transition from first to second order takes place at such $[Cu^{2+}]$ that on average only about one copper ion is present per polydentate coil. Consequently, dimerization will also be retarded because it often requires reaction between Cu(I) ions complexed in different polydentate coils.

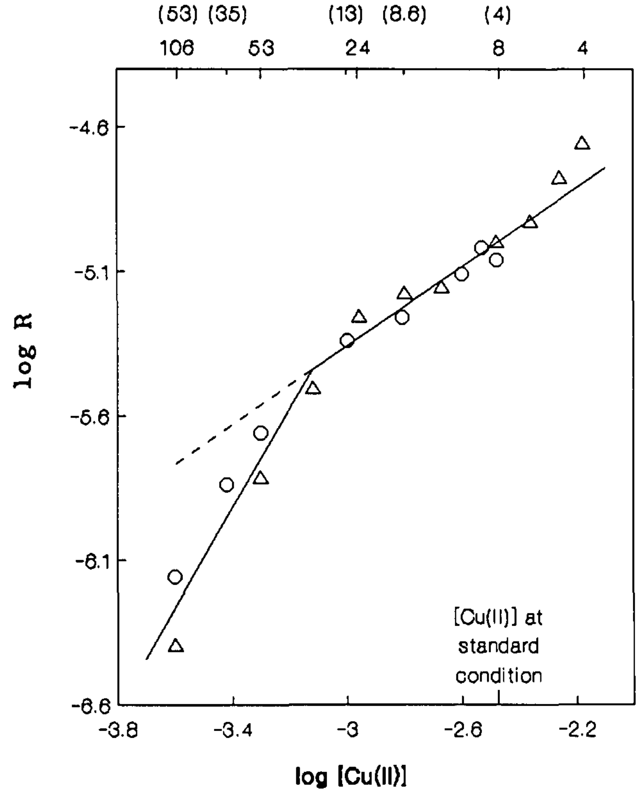


Figure 8 Plot of log *R versus* log[Cu(II)] under standard conditions for PS-Im with: (△) $\alpha = 0.17$ and [imidazole] $= 26.6 \times 10^{-3}\,mol\,dm^{-3}$; (○) $\alpha = 0.05$ and [imidazole] $= 13.3 \times 10^{-3}\,mol\,dm^{-3}$. (Ligand/Cu values for $\alpha = 0.17$ are indicated at the top of 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)] is in $mol\,dm^{-3}$

Effect of solvent system on reaction rate

As shown in *Figure 9* the reaction rates with Cu(II)–PS-Im or Cu(II)–NMIm are smaller for toluene/isopropanol 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/isopropanol. Obviously, this phenomenon is primarily related to either methanol or isopropanol being used as cosolvent, rather than to expansion or contraction of the polymeric ligands in solution. In fact, the same specific viscosities (η_{sp}) are observed for solutions of polymeric ligands in either toluene/MeOH or toluene/isopropanol (see *Figure 4*). So, coordinated methanol seems to be more accessible to substitution by substrate than isopropanol.

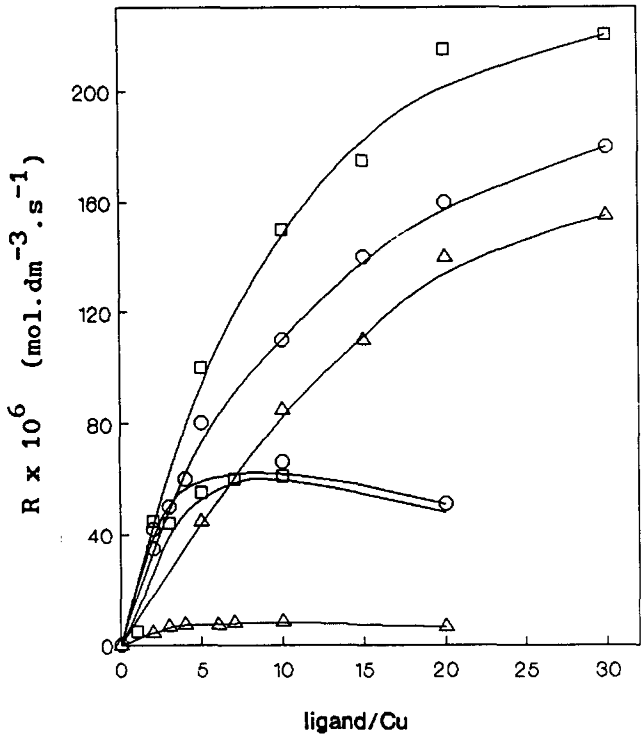


Figure 9 Steady-state reaction rate as a function of ligand/Cu ratio under standard conditions in different solvent systems. For Cu(II)–NMIm (upper curves): (△) toluene/isopropanol (13/2 v/v); (□) toluene/MeOH (13/2 v/v); (○) oDCB/MeOH (13/2 v/v). For Cu(II)–PS-Im (lower curves): (△) toluene/isopropanol (13/2 v/v) and $\alpha = 0.23$; (□) toluene/MeOH (13/2 v/v) and $\alpha = 0.23$; (○) oDCB/MeOH (13/2 v/v) and $\alpha = 0.17$

Fortunately, methanol gives 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 7.0% is found in toluene/MeOH as compared to 5% in toluene/isopropanol in *Figure 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.

CONCLUDING REMARKS

For Cu(II)–PS-Im complexes an increase of the ligand/copper ratio is accompanied by a transformation of dinuclear copper complexes into mononuclear ones, especially $Cu(PS\text{-}Im)_4^{2+}$, which is favourable for higher catalytic activity and better specificity for PPO formation. The good specificity found in the case of Cu(II)–NMIm complexes is also observed for the Cu(II)–PS-Im catalytic system. At a slight expense of catalytic specificity, a much higher reaction rate is observed in toluene/MeOH than in toluene/isopropanol. Therefore, the solvent mixture toluene/MeOH (13/2 v/v) is preferred for future studies on immobilization of polymer-bound imidazole–copper(II) complexes as catalysts for the oxidation coupling polymerization of DMP.

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REFERENCES

1 Verlaan, J. P. J., Bootsma, J. P. C. and Challa, G. *J. Mol. Catal.* 1982, **14**, 211
2 Verlaan, J. P. J., Bootsma, J. P. C., Koning, C. E. and Challa, G. *J. Mol. Catal.* 1983, **18**, 159
3 Koning, C. E., Brinkhuis, R., Wevers, R. and Challa, G. *Polymer* 1987, **28**, 2310
4 Meinders, H. C. and Challa, G. *J. Mol. Catal.* 1980, **7**, 321
5 Sundberg, R. G. and Martin, R. B. *Chem. Rev.* 1974, **74**, 471
6 Verlaan, J. P. J., Zwiers, R. and Challa, J. *J. Mol. Catal.* 1983, **19**, 223
7 Challa, G., Schouten, A. J., ten Brinke, G. and Meinders, H. C. in 'Modification of Polymers', (Eds. C. E. Carraher Jr and M. Tsuda), ACS Symp. Ser. 1980, **121**, 7
8 Chen, W. and Challa, G. *Eur. Polym. J.* in press
9 Petrak, K. L. *J. Polym. Sci., Polym. Lett. Edn.* 1978, **16**, 393
10 Breemhaar, W., Meinders, H. C. and Challa, G. *J. Mol. Catal.* 1981, **10**, 33
11 Reedijk, J. *Transition Met. Chem.* 1981, **6**, 195
12 Koning, C. E., Eshuis, J. J. W., Viersen, F. J. and Challa, G. *React. Polym.* 1986, **4**, 293
13 Koning, C. E., Jongsma, T., Brinkhuis, R. and Challa, G. *React. Polym.* 1988, **8**, 255
14 Schouten, A. J., Noordegraaf, D., Jekel, A. P. and Challa, G. *J. Mol. Catal.* 1979, **5**, 331
15 Challa, G. *J. Mol. Catal.* 1983, **21**, 1
16 Challa, G. *Makromol. Chem. Suppl.* 1980, **5**, 70
17 Viersen, F. J., Challa, G. and Reedijk, J. *Polymer* in press
18 Koning, C. E., Viersen, F. J. and Challa, G. *J. Mol. Catal.* 1988, **44**, 245