

Copper(II) complexes of "polystyrene-bound DMAP" : synthesis, structure and catalytic activity in the oxidative coupling of 2,6-dimethylphenol

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COPPER(II) COMPLEXES OF “POLYSTYRENE-BOUND DMAP” *: SYNTHESIS, STRUCTURE AND CATALYTIC ACTIVITY IN THE OXIDATIVE COUPLING OF 2,6-DIMETHYLPHENOL

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The oxidative coupling of 2,6-dimethylphenol by Cu(II) complexes of “polystyrene-bound DMAP” was studied. The polymer was prepared by radical copolymerization of styrene and 4-(N-methyl-N-p-vinylbenzylamino)pyridine (I). Monomer (I) was prepared as described by Tomoi et al. [7]. By purifying the monomer by column chromatography instead of distillation, however, we succeeded in raising its yield by some 20%. Catalytic experiments supported by UV and EPR experiments revealed that in the catalytically active solution an equilibrium exists between dinuclear and mononuclear Cu(II) complexes. The concentration of the catalytically most active, mononuclear species Cu(II)(ligand)₄(OH)Cl increases on enhancing the ligand/Cu ratio and decreases on addition of an excess of copper-coordinating hydroxide ions. From this structural point of view the polymeric catalyst proved to behave just like low molar mass Cu(II)–DMAP complexes, although the mononuclear polymeric catalyst is more stable because of a polydentate effect. From the difference in reaction order in copper for unbound and polystyrene-bound DMAP catalysts, it was concluded that for the reoxidation step dimerization of Cu(I) complexes is needed, whereas mononuclear Cu(II) complexes are the most active species for the oxidation of DMP. The mentioned dimerization is promoted by the polymer chain. The specificity of the polystyrene-bound DMAP catalyst for formation of polyphenyleneoxide exceeds 95%.

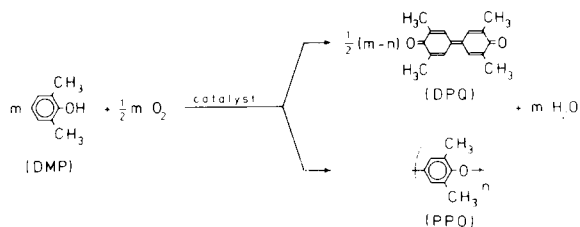
INTRODUCTION

Recently a study was reported on the catalysis of the oxidative coupling of 2,6-dimethyl-

phenol (DMP) by copper(II) complexes of 4-(N,N-dimethylamino)pyridine (DMAP) [1]. The investigated catalyst proved to be very active and specific for the formation of moderately high molar mass “polyphenyleneoxide” (PPO). In addition a small amount of the undesired byproduct “diphenoquinone” (DPQ) is formed (Scheme 1).

* Poly[styrene-co-4-(N-methyl-N-p-vinylbenzylamino)pyridine].

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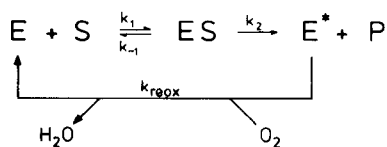
Scheme 1

Usually the oxidative coupling reaction can be described by the Michaelis–Menten scheme [2,3] as given in Scheme 2. In Scheme 2, E stands for the Cu(II) complex, E* for the Cu(I) complex, S for the substrate DMP, and P for the products DPQ and PPO. It is known that for the low molar mass Cu(II)–DMAP catalyst the reoxidation of Cu(I) to Cu(II) is rate determining [1,4] and no Michaelis–Menten type of reaction kinetics in terms of substrate is observed. For Cu(II) complexes of polystyrene-bound DMAP, however, Scheme 2 is valid [4]. In this case the oxidation of DMP is rate determining (k_2 in Scheme 2). The enhancement of k_{reox} on attaching a low molar mass Cu(II) ligand to a polystyrene chain was more often observed, and was in general ascribed to the non-polar character of the polymer backbone [5,6].

For the polystyrene-bound analogue of DMAP, plots of reciprocal reaction rates versus reciprocal substrate concentrations yield straight lines intersecting the y -axis according to the following equation [4]:

$$\frac{1}{R} = \frac{1}{k_2[E]_0} + \frac{K_m}{k_2[E]_0[S]_0} \quad (1)$$

in which R is the dioxygen consumption rate, k_2 the rate-determining rate constant, $[E]_0$



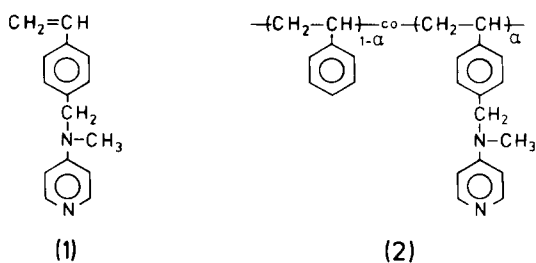
Scheme 2

and $[S]_0$ the initial concentrations of copper(II) salt and DMP, respectively, and $K_m = (k_{-1} + k_2)/k_1$ the Michaelis constant.

Our investigations with the low molar mass catalyst [1] showed that in solution mononuclear and dinuclear Cu(II)–DMAP complexes are simultaneously present. For relatively low DMAP/Cu ratios the complexes were found to be dinuclear. On addition of an excess of strong-base DMAP ligands, however, these complexes were transformed into mononuclear species, even in the presence of strongly bridging hydroxide ions. Furthermore it was concluded that the catalytically most active species was Cu(II)(DMAP)₄Cl(OH). It is the aim of the present study to investigate whether similar observations are made with Cu(II) complexes of poly[styrene-co-4-(*N*-methyl-*N*-*p*-vinylbenzylamino)pyridine](**2**) (Scheme 3).

As with the low molar mass analogue DMAP, additional spectroscopic studies on the structure of the complexes in solution will explain the catalytic results.

Verlaan et al. [4] synthesized their polymeric Cu(II) ligand (**2**) by partial chloromethylation of polystyrene followed by a coupling reaction with a slight excess of the sodium salt of 4-(*N*-methylamino)pyridine according to Tomoi et al. [7]. However, this method has at least two significant draw-backs. In the first place unreacted chloromethyl groups may give rise to inter- or intramolecular crosslinking reactions with styrene units. In this reaction HCl is formed, which is harmful for the catalyst. In the second place the mentioned



Scheme 3

chloromethyl groups may form quaternary ammonium salts with the basic pyridine ligands of the same or another polymer chain resulting in a lowering of the effective ligand/Cu ratio as well as in crosslinking. Both crosslinking and the distortion of the optimum ligand/Cu ratio lead to a deactivation of the polymer catalyst. For this reason we decided to follow the route via the monomer 4-(*N*-methyl-*N*-*p*-vinylbenzylamino)pyridine (**1**) synthesized according to Tomoi et al. [7]. The desired polymer (**2**) can be obtained by radical copolymerization of pure monomer (**1**) with styrene. In this way the disadvantages of eventually unreacted chloromethyl groups mentioned above are circumvented and we expect the Cu(II) complex of our polymer (**2**) to be at least as active as the polymer catalysts synthesized by Verlaan et al. [4].

Another great advantage of working with monomer (**1**) is the ease and accuracy with which the chain loading (α) of the polymeric catalysts with DMAP units can be varied. Furthermore this approach seems more appropriate for future grafting of (polystyrene-bound DMAP)-copper catalysts on small silica particles by copolymerization of monomer (**1**) and styrene. Attempts to achieve this by modifying linear polystyrene grafted on hydrophilic silica were not successful. The chloromethylation and the subsequent reaction with $\text{NaN}(\text{CH}_3)(\text{C}_5\text{H}_4\text{N})$ failed.

EXPERIMENTAL

Materials

1,2-Dichlorobenzene, KOH, LiOH and $\text{CuCl}_2 \cdot 2\text{H}_2\text{O}$ were from Merck and analytically pure. The copper salt and the hydroxides were used as methanolic solutions in which the methanol was of Uvasol quality from Merck. 2,6-Dimethylphenol was from Aldrich and was purified by recrystallization

from *n*-hexane. 4-(*N,N*-Dimethylamino)pyridine (DMAP) was from Aldrich and used without further purification.

Synthesis of 4-(*N*-methyl-*N*-*p*-vinylbenzylamino)pyridine

Monomer (**1**) (6.6 g, 29.5 mmol) was mainly synthesized as described by Tomoi et al. [7]. However, the formation of the sodium salt of 4-(*N*-methylamino)pyridine and the subsequent reaction with *p*-chloromethylstyrene were not carried out in DMF but in more volatile, dry THF. The synthesis of *p*-chloromethylstyrene (12.3 g, 81 mmol) was carried out as described [7]. The synthesis and the purification of monomer (**1**) were carried out in the dark. After separation of sodium chloride by filtration the THF was evaporated from the filtrate. The resulting viscous liquid was diluted with dichloromethane and this solution was washed with demineralized water, dried over anhydrous MgSO_4 , and concentrated. The oily residue was again dissolved in a minimum volume of dichloromethane and the solution was poured upon a chromatography column (60 g Al_2O_3 ; 1.5 g H_2O ; Aktivitätstufe II; column dimensions 20×1.5 cm). First impurities were eluted with dichloromethane and subsequently the monomer was eluted slowly with more CH_2Cl_2 . This CH_2Cl_2 fraction was treated with activated charcoal. After filtration the CH_2Cl_2 was evaporated under vacuum at 30°C . The resulting viscous oil slowly crystallized at room temperature. The product was characterized by $^1\text{H-NMR}$ and IR and proved to be pure. The yield of pure monomer (**1**) based on 4-(*N*-methylamino)pyridine and *p*-chloromethylstyrene was 69%. The method described by Tomoi et al. [7], involving purification by distillation under reduced pressure in the presence of DPPH (diphenylpicrylhydrazyl), gave the pure monomer in a yield of only 47%.

Copolymerization of styrene and 4-(N-methyl-N-p-vinylbenzylamino)pyridine

Polymer-supported 4-(*N*-benzyl-*N*-methylamino)pyridine was prepared by radical copolymerization using AIBN as an initiator: 5.276 g (23.5 mmol) of monomer (**1**) and 7.339 g (70.5 mmol) of freshly distilled styrene were allowed to polymerize in the presence of 1 mol% (based on total monomer) of AIBN under nitrogen for 40 h at 80°C in 38.1 g of toluene. The polymer was precipitated in petroleum-ether 40–60 and reprecipitated twice from chloroform in petroleum-ether 40–60. Yield: 8.913 g of slightly yellow polymer (70%). The polymer was characterized by IR and elemental analysis. The mole fraction of monomer (**1**) units in the copolymer was $\alpha = 0.226$. The number-average molar mass, \overline{M}_n , was determined in chloroform with a Knauer membrane osmometer:

$$\overline{M}_n = 4 \times 10^4 \text{ g mol}^{-1}.$$

Oxidative coupling

The following standard reaction conditions were used: $T = 298.2 \text{ K}$, $[\text{Cu(II)}] = 8.3 \times 10^{-4} \text{ mol dm}^{-3}$, $[\text{DMP}] = 0.06 \text{ mol dm}^{-3}$, $P_{\text{O}_2} = 101.3 \text{ kPa}$, total reaction volume = 0.015 dm^3 , solvent mixture 1,2-dichlorobenzene/methanol = 13/2 (v/v). These conditions are as before [1,4], except for $[\text{Cu(II)}]$, which was reduced by 75% because of the extremely high activity of the catalyst based on polymer (**2**). The polymeric catalyst was prepared *in situ* by dissolving the polymer ligand (**2**) in the solvent mixture and adding methanolic solutions of $\text{CuCl}_2 \cdot 2\text{H}_2\text{O}$ and, if desired, KOH or LiOH. The cylindrical reaction vessel was connected to an automatic gas burette with pure dioxygen [8]. The reaction mixture was saturated with dioxygen and the oxidative coupling was started by addition of DMP. The vessel was vigorously shaken in a thermostatted bath, and the dioxygen consumption

was recorded at constant pressure as a function of reaction time. The steady-state reaction rate R was calculated from the maximum slope of the dioxygen consumption curve.

Determination of catalytic specificity of the complexes

In order to determine the catalytic specificity for PPO formation some reactions were run to completion and aliquots of the reaction mixtures were diluted with solvent mixture. DPQ concentrations were determined with a PYE Unicam SP-8-200 UV/Vis spectrophotometer at 426 nm ($\epsilon = 61,000 \text{ dm}^3 \text{ mol}^{-1} \text{ cm}^{-1}$). From these data the percentage of DMP that had been transformed into DPQ was calculated, and thus the PPO yield became known.

Spectroscopic analyses of the polymeric Cu(II) complexes

UV spectra of solutions of the polymeric Cu(II) complexes (standard conditions, except $[\text{Cu(II)}] = 3.32 \times 10^{-3} \text{ mol dm}^{-3}$, see earlier) were recorded on a PYE Unicam SP-8-200 UV/Vis spectrophotometer at 298.2 K. EPR spectra of frozen solutions of the complexes were recorded on a Varian E4 spectrophotometer (77 K). (Standard conditions with $[\text{Cu(II)}] = 3.32 \times 10^{-3} \text{ mol dm}^{-3}$.)

RESULTS

Catalytic experiments

Catalytic experiments with unbound Cu(II)–DMAP complexes showed that copper salts with copper-coordinating counter ions such as Cl^- should be used in order to have maximum activity [1]. It is assumed that this is also valid for the polymeric catalyst based on polymer (**2**). As in the case of unbound Cu(II)–DMAP complexes, the copper com-

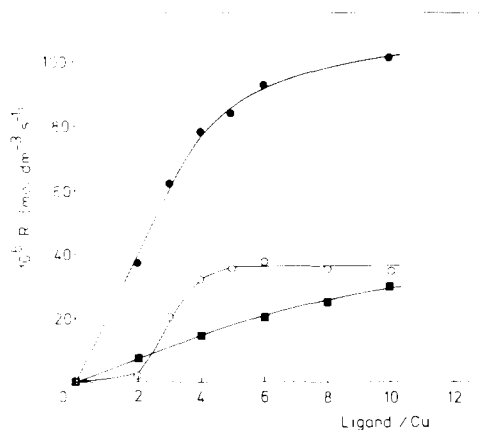


Fig. 1. Dioxygen-consumption rate R as a function of the ratio ligand/Cu. Standard conditions (see Experimental). (○) polymer (2) ($\alpha = 0.226$), $(\text{OH}/\text{Cu})_0 = 0$; (●) polymer (2) ($\alpha = 0.226$), $(\text{OH}/\text{Cu})_0 = 1$; (■) DMAP, $(\text{OH}/\text{Cu})_0 = 1$.

plexes of polymer (2) proved to be catalytically active without initial hydroxide addition, although the dioxygen consumption did not start immediately after addition of DMP to the catalyst solution and significant initiation periods were observed (see further on).

In Fig. 1 (○) the reaction rate of the oxidative coupling of DMP with the polymer (2)-based catalyst and $(\text{OH}/\text{Cu})_0 = 0$ is given as a function of the ligand/Cu ratio. For a Michaelis-Menten type of reaction kinetics, a dioxygen-consumption curve like curve a in

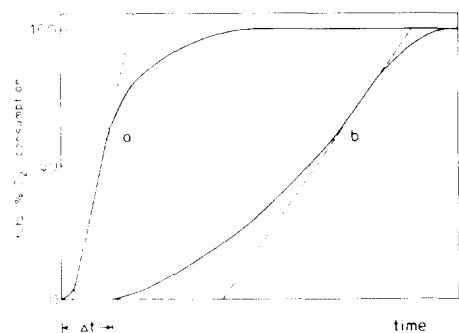


Fig. 2. Schematic dioxygen-consumption curves for polymer (2)-based Cu(II) catalysts. (a) $(\text{OH}/\text{Cu})_0 = 1$ (Michaelis-Menten type curve); (b) $(\text{OH}/\text{Cu})_0 = 0$.

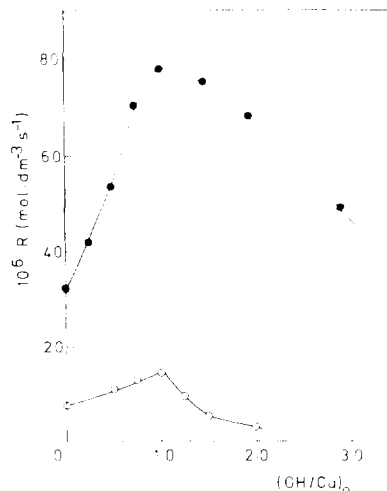


Fig. 3. Dioxygen-consumption rate R as a function of $(\text{OH}/\text{Cu})_0$. Standard conditions with ligand/Cu = 4. (○) DMAP-based catalyst; (●) polymer (2)-based catalyst ($\alpha = 0.226$).

Fig. 2 is expected. However, for the experiments with $(\text{OH}/\text{Cu})_0 = 0$ curves like curve b were observed. As indicated in Fig. 2, the reaction rates plotted in Fig. 1 were determined from the maximum slopes of the dioxygen-consumption curves, which were attained at about 60% of the total conversion for $(\text{OH}/\text{Cu})_0 = 0$.

From Fig. 3 it can be seen that the catalytic activity of our polymeric catalyst can be enhanced significantly by hydroxide addition, with optimum activity at $(\text{OH}/\text{Cu})_0 = 1$. For comparison the situation for the low molar mass Cu(II)-DMAP catalyst is given as well. Consequently, R was also measured as a function of the ligand/Cu ratio for $(\text{OH}/\text{Cu})_0 = 1$. The O_2 -consumption curves were like curve a in Fig. 2. The results are depicted in Fig. 1 (●). The accelerating effect of hydroxide is clear. Striking are the bends in the curves at ligand/Cu ≈ 4 for both experiments with and without initial hydroxide addition. The situation for the low molar mass Cu(II)-DMAP catalyst is also given in Fig. 1 (■).

In our paper on low molar mass Cu(II)-DMAP catalysts [1] the catalytic activity in

experiments with $(\text{OH}/\text{Cu})_0 = 0$ was explained by hydroxide production by the basic ligands out of traces of water present in the reaction mixture. The following experiment is an indication that this actually happens.

A reaction mixture with $(\text{OH}/\text{Cu})_0 = 0$, ligand/Cu = 6, $[\text{Cu}(\text{II})] = 0.83 \text{ mmol dm}^{-3}$ and the standard amount of DMP was allowed to react completely. The initiation period of the reaction was 1020 s (see further on and see Table 3) and the maximum dioxygen-consumption rate R was $38.5 \times 10^{-6} \text{ mol dm}^{-3} \text{ s}^{-1}$. The dioxygen-consumption curve was like curve b in Fig. 2. After completion a new standard amount of DMP was added to the reaction mixture. This time the reaction started within 30 s. The O_2 -consumption curve was like curve a in Fig. 2 and the maximum rate was $58.5 \times 10^{-6} \text{ mol dm}^{-3} \text{ s}^{-1}$. In view of Fig. 3 this might be explained by the initial presence of hydroxide ions in the reaction mixture in case of the second run.

For low molar mass Cu(II)–DMAP complexes the species $\text{Cu}(\text{DMAP})_4(\text{OH})\text{Cl}$ was found to be the catalytically most active one [1]. As preliminary spectroscopic studies with

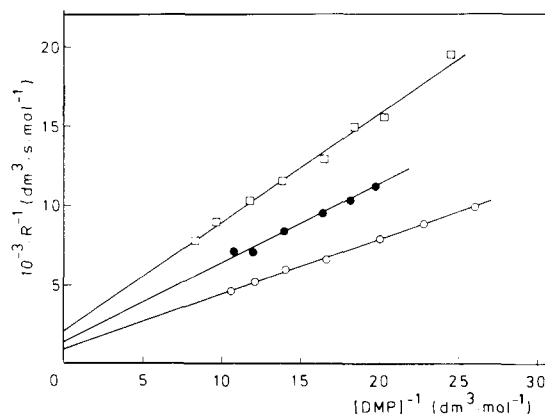


Fig. 4. Lineweaver–Burk plots for the Cu(II)–polymer (2) catalyst ($\alpha = 0.226$) under standard conditions, except $[\text{Cu}(\text{II})]$. (\square) ligand/Cu = 4, $(\text{OH}/\text{Cu})_0 = 1$, $[\text{Cu}(\text{II})] = 0.83 \text{ mmol dm}^{-3}$; (\bullet) ligand/Cu = 2, $(\text{OH}/\text{Cu})_0 = 1$, $[\text{Cu}(\text{II})] = 3.32 \text{ mmol dm}^{-3}$; (\circ) ligand/Cu = 4, $(\text{OH}/\text{Cu})_0 = 1$, $[\text{Cu}(\text{II})] = 1.66 \text{ mmol dm}^{-3}$.

the copper catalyst based on polymer (2) also showed the existence of species CuN_4 (where N = ligand), it was decided to carry out part of the kinetic analyses with ligand/Cu = 4. In order to be able to compare the catalytic activity of our polymer (2)-based catalyst with the activity of the polymeric “DMAP”–

TABLE 1

Kinetic parameters for polystyrene-bound DMAP copper catalysts

Chain loading (α) of polymer (2)	$[\text{Cu}(\text{II})]$ (mmol dm^{-3})	Ligand/Cu	k_2 (s^{-1})	K_m^{-1} ($\text{dm}^3 \text{ mol}^{-1}$)
0.031 ^a	3.32	2	0.12	5.5
0.056 ^a	3.32	2	0.10	4.1
0.086 ^a	3.32	2	0.14	4.2
0.159 ^a	3.32	2	0.14	4.2
0.173 ^a	3.32	2	0.14	3.7
0.226 ^b	3.32	2	0.22	2.8
0.226 ^b	3.32	4	– ^c	– ^c
0.226 ^b	1.66	4	0.57	3.1
0.226 ^b	0.83	4	0.51	3.6

Standard conditions with $(\text{OH}/\text{Cu})_0 = 1$, except catalyst concentration (see Experimental).

^a Prepared by Verlaan et al. [4] by reaction of $\text{NaN}(\text{CH}_3)(\text{C}_5\text{H}_4\text{N})$ with chloromethylated polystyrene.

^b Prepared by radical copolymerization of monomer (1) and styrene.

^c Dioxygen-consumption rates exceed the measuring range of the automatic gas burette.

copper catalyst of Verlaan et al. [4], another part of the kinetic work was performed with ligand/Cu = 2, as Verlaan et al. applied. Lineweaver–Burk plots of R^{-1} versus $[\text{DMP}]^{-1}$ were constructed for the catalyst based on polymer (2) for ligand/Cu ratios of 2 and 4 and different copper concentrations (Fig. 4). In all cases $(\text{OH}/\text{Cu})_0 = 1$. Under these conditions all double-reciprocal plots yield straight lines intersecting the y -axis (see Introduction). All kinetic parameters calculated from Fig. 4 are presented in Table 1. For comparison the parameters for some polymeric Cu(II)–DMAP catalysts prepared by Verlaan et al. [4] are given as well.

Catalytic specificity of the polymeric Cu(II)–DMAP complexes

In Table 2 the percentage of DMP that is transformed into PPO is given as a function

of several parameters for the polymer (2)-based catalyst. For comparison some data for the low molar mass Cu(II)–DMAP catalyst are given as well [1]. The general trends shown in Table 2 are the following:

- (1) Addition of hydroxide ($(\text{OH}/\text{Cu})_0 = 1$) promotes PPO formation.
- (2) A higher ligand/Cu ratio yields more PPO (up to a maximum of 96–97%).
- (3) A higher catalyst concentration yields more PPO.

The initiation period of the oxidative coupling reaction

The initiation period Δt of the reaction has been defined as the time interval between DMP addition and the start of the dioxygen consumption [1]. When hydroxide is initially added, Δt only amounts to a few seconds. If

TABLE 2

Specificity for PPO production as a function of the ligand/Cu ratio, $(\text{OH}/\text{Cu})_0$, $[\text{Cu(II)}]$ and the nature of the DMAP-based Cu(II) catalyst

Nature of ligand	Ligand/Cu	$(\text{OH}/\text{Cu})_0$	$[\text{Cu(II)}]$ (mmol dm ⁻³)	% PPO
Polymer (2); $\alpha = 0.226$	1	1	3.32	80
	2	1	3.32	90
	3	1	3.32	93
	4	1	3.32	95
	5	1	3.32	96
	6	1	3.32	96
	4	0	3.32	93
	7	0	3.32	97
	10	0	3.32	97
	4	1	1.66	89
	2	0	0.83	56
	3	0	0.83	72
	4	0	0.83	81
	4	1	0.83	88
	10	0	0.83	91
DMAP	10	1	0.83	92
	2	0	3.32	80
	2	1	3.32	91
	4	0	3.32	94
	4	1	3.32	95
	8	0	3.32	96
	8	1	3.32	96

Standard conditions unless otherwise indicated.

TABLE 3

Initiation period Δt for the copper complexes of polymer (2) ($\alpha = 0.226$) and DMAP as a function of ligand/Cu; $(\text{OH}/\text{Cu})_0 = 0$; standard conditions unless otherwise indicated)

Nature of ligand	Ligand/Cu	[Cu(II)] (mmol dm ⁻³)	Δt (s)	
Polymer (2)	2	0.83	4880	
	3	0.83	2910	
	4	0.83	2660	
	5	0.83	2110	
	6	0.83	1020	
	8	0.83	1250	
	10	0.83	910	
	4	3.32	$\sim 1^b$	
	DMAP ^a	4	3.32	12
		4	1.66	280
4		0.83	660	
4		3.32	2^b	

$(\text{OH}/\text{Cu})_0 = 0$; standard conditions unless otherwise indicated.

^a Ref. [1].

^b $(\text{OH}/\text{Cu})_0 = 1$.

$(\text{OH}/\text{Cu})_0 = 0$, however, high values of Δt are observed. Some Δt values for the polymer (2)-based catalyst are listed in Table 3. For comparison some data for the low molar mass analogue are listed as well.

Table 3 shows the following general trends:

- (1) Δt is reduced on enhancing the ligand/Cu ratio, thus on enhancing the basicity of the reaction medium.
- (2) Δt decreases when the catalyst concentration is enhanced.
- (3) In comparison with the low molar mass Cu(II)-DMAP catalyst the Δt values for the polymer (2)-based catalyst are higher.

Structure of the complexes in solution

As with the low molar mass Cu(II)-DMAP catalysts it is our intention to explain the catalytic results with the polymer (2)-based catalyst from the structure of the active complexes in solution. Therefore a spectroscopic

analysis consisting of UV/Vis and EPR experiments was carried out.

UV/Visible spectroscopy

As UV/Vis spectra may give an indication of the composition of the complexes, these were recorded of solutions of copper complexes based on polymer (2) for varying ligand/Cu ratios. Standard conditions were used with $[\text{Cu(II)}] = 3.32 \times 10^{-3} \text{ mol dm}^{-3}$ and no DMP was added. As for the low molar mass Cu(II)-DMAP complexes the d-d absorptions of the polymer (2)-based copper complexes are located in the visible region. In Fig. 5 the d-d absorption spectra of the copper complexes of polymer (2) are drawn for ligand/Cu ratios varying from 0 to 10. In this case no hydroxide was added. Striking are the double maxima around 800 nm for ligand/Cu ≤ 4 and the appearance of an isosbestic point for ligand/Cu ≥ 1 suggesting a change from one coloured species into another [9]. For ligand/Cu ≤ 1.5 , there is a build-up of one of these species. Similar phenomena were observed for the low molar mass Cu(II)-DMAP catalysts [1], although in that case the isosbestic point was found for ligand/Cu ≥ 2 and the double maxima were found for ligand/Cu ≤ 6 .

In Fig. 6 the d-d absorption curves of the Cu(II)-polymer (2) complexes are given for $(\text{OH}/\text{Cu})_0 = 1$ and ligand/Cu ratios varying from 0 to 10. Now, the presence of double maxima around 800 nm for ligand/Cu ≤ 1.5 and the presence of an isosbestic point for ligand/Cu ≥ 0.5 are striking. For the low molar mass analogue with $(\text{OH}/\text{Cu})_0 = 1$ an isosbestic point was found for ligand/Cu ≥ 1 and double maxima were observed for ligand/Cu ≤ 2 [1].

As for the low molar mass analogue the single-absorption maxima in the spectra of Figs. 5 and 6 are attributed to mononuclear species with the general formula $\text{Cu}(\text{DMAP})_n\text{X}_2$ with X = OH⁻ or Cl⁻ and $n \geq 4$. In Fig. 7 the absorbances of these species are

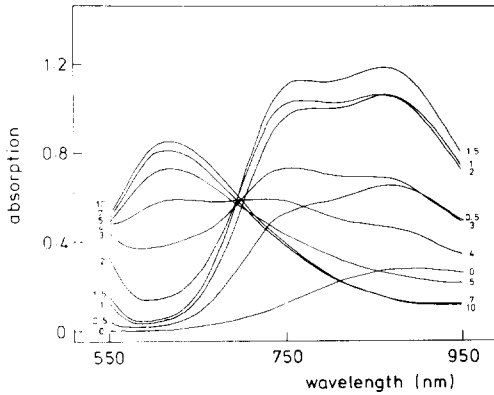


Fig. 5. d-d Absorption spectra for various ligand/Cu ratios for the system Cu(II)-polymer (2) ($\alpha = 0.226$). Standard conditions with $[\text{Cu(II)}] = 3.32 \times 10^{-3} \text{ mol dm}^{-3}$ and $(\text{OH}/\text{Cu})_0 = 0$. No DMP was added. Ligand/Cu ratios are indicated in the figure.

given as a function of ligand/Cu ratio. Both curves for $(\text{OH}/\text{Cu})_0 = 0$ and 1 show a bend, which should be compared with the bends in the curves of R vs. ligand/Cu ratio for the correspondig complexes (Fig. 1).

EPR spectroscopy

As mononuclear copper complexes are EPR-active species and dinuclear copper

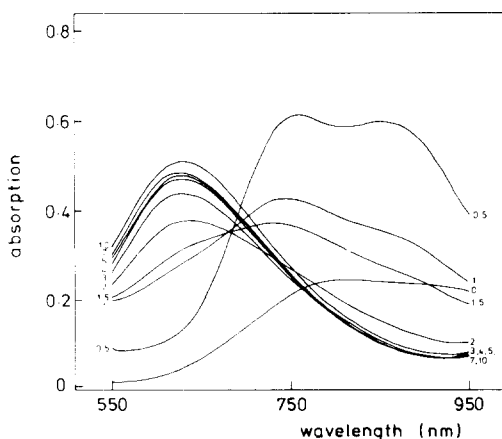


Fig. 6. d-d Absorption spectra for various ligand/Cu ratios for the system Cu(II)-polymer (2) ($\alpha = 0.226$). Standard conditions with $[\text{Cu(II)}] = 3.32 \times 10^{-3} \text{ mol dm}^{-3}$ and $(\text{OH}/\text{Cu})_0 = 1$. No DMP was added. Ligand/Cu ratios are indicated in the figure.

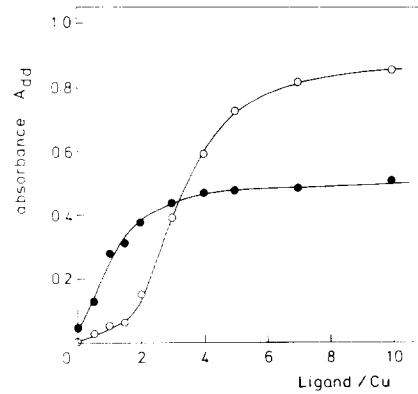


Fig. 7. Absorbance of mononuclear complexes as a function of the ligand/Cu ratio as derived from Figs. 5 and 6. Standard conditions with $[\text{Cu(II)}] = 3.32 \times 10^{-3} \text{ mol dm}^{-3}$ and without DMP. (O) $(\text{OH}/\text{Cu})_0 = 0$; $\lambda_{\text{max,mono}} = 616 \text{ nm}$; (●) $(\text{OH}/\text{Cu})_0 = 1$; $\lambda_{\text{max,mono}} = 623 \text{ nm}$.

species are often EPR-silent [10] or show $S = 1$ spectra, one should be able to distinguish between mono- and dinuclear copper com-

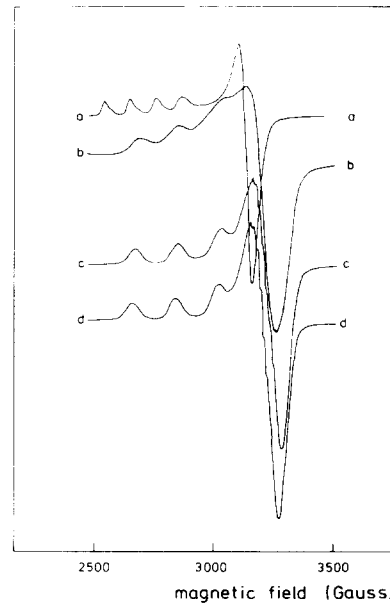


Fig. 8. EPR spectra of Cu(II)-polymer (2) complexes ($\alpha = 0.226$) at standard conditions with $[\text{Cu(II)}] = 3.32 \times 10^{-3} \text{ mol dm}^{-3}$ and $(\text{OH}/\text{Cu})_0 = 0$. No DMP was added. (a) ligand/Cu = 0.5 and receiver gain (RG) = 2.0×10^3 ; (b) ligand/Cu = 2 and RG = 1.5×10^4 ; (c) ligand/Cu = 4 and RG = 2.5×10^3 ; (d) ligand/Cu = 7 and RG = 2.5×10^3 .

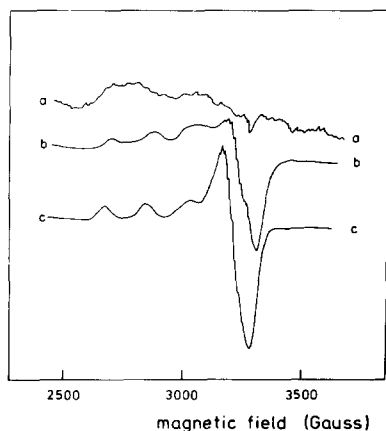


Fig. 9. EPR spectra of Cu(II)-polymer (2) complexes ($\alpha = 0.226$) at standard conditions with $[\text{Cu(II)}] = 3.32 \times 10^{-3} \text{ mol dm}^{-3}$ and $(\text{OH}/\text{Cu})_0 = 1$. No DMP was added. (a) ligand/Cu = 0.5 and $\text{RG} = 1 \times 10^5$; (b) ligand/Cu = 2 and $\text{RG} = 2.5 \times 10^4$; (c) ligand/Cu = 4 and $\text{RG} = 1.5 \times 10^4$.

plexes by performing an EPR-study. EPR spectra were recorded in frozen 1,2-dichlorobenzene/methanol solutions without DMP.

Some typical spectra are given in Figs. 8 and 9 as an illustration. Please note the nitrogen super-hyperfine structure in the spectra c and d in Fig. 8 and the spectra b and c in Fig. 9. In order to compare relative EPR intensities one should notice the different receiver gains used for the spectra. These are given in the figure captions. Other experimental variables were kept constant.

The systems under investigation are listed in Table 4 together with their EPR parameters. As can be seen from this table the parameters for the systems with $(\text{OH}/\text{Cu})_0 = 0$ and ligand/Cu ≤ 1 are all alike: the only detectable species is the species that is also present in a solution of $\text{CuCl}_2 \cdot 2\text{H}_2\text{O}$, and no nitrogen super-hyperfine splitting is observed. For systems with ligand/Cu ≥ 4 , the parameters are typical for a species CuN_4 [11] and nitrogen super-hyperfine splitting is observed. The system with ligand/Cu = 2 is a kind of change-over system.

Although the EPR spectra were not in-

TABLE 4

EPR parameters of investigated solutions of copper complexes of polymer (2)

Ligand/Cu	$(\text{OH}/\text{Cu})_0$	N-N hyperfine splitting (G)	g_{\perp}	g_{\parallel}	A_{\parallel} (G)
0.0	0	ND ^a	2.08	2.42	108
0.5	0	ND ^a	2.09	2.43	109
1.0	0	ND ^a	2.09	2.43	109
2.0	0	ND ^a	2.06	2.25	165
4.0	0	14	2.04	2.25	180
5.0	0	14	2.04	2.24	180
7.0	0	14	2.04	2.24	180
10.0	0	14	2.04	2.24	180
0.0	1	ND ^a	2.08	2.42	110
0.5	1	ND ^a	ND ^b	ND ^b	ND ^b
1.0	1	ND ^a	2.08	ND ^a	110
2.0	1	13.8	2.04	2.24	183
4.0	1	13.5	2.04	2.24	183
5.0	1	13.5	2.05	2.24	183
7.0	1	14	2.05	2.25	183
10.0	1	14	2.04	2.23	183

Standard conditions with $[\text{Cu(II)}] = 3.32 \times 10^{-3} \text{ mol dm}^{-3}$; no addition of DMP.

^a ND = not detectable.

^b A very, very small EPR signal is observed.

tegrated it appeared that the relative EPR intensity for the species CuN_4 generally increased on enhancing the ligand/Cu ratio. Of course, the EPR intensity of the species originally present in the $\text{CuCl}_2 \cdot 2\text{H}_2\text{O}$ solution decreased on addition of ligands.

For the system with $(\text{OH}/\text{Cu})_0 = 1$ and ligand/Cu ≤ 1 the EPR intensity is strongly reduced with respect to the systems without OH^- addition. The detectable EPR parameters agree with those for the $\text{CuCl}_2 \cdot 2\text{H}_2\text{O}$ solution and there is no nitrogen super-hyperfine splitting. However, when ligand/Cu ≥ 2 nitrogen super-hyperfine splitting is observed and the EPR parameters of the main species, again, are typical for CuN_4 . For these systems the EPR intensity of the species CuN_4 in general also increases on addition of more ligands, although the intensity is much weaker in comparison with the systems with $(\text{OH}/\text{Cu})_0 = 0$. The EPR intensity is extremely reduced on addition of still more hydroxide. The following may serve as an illustration. Let us define the EPR intensity of the system with ligand/Cu = 10 and $(\text{OH}/\text{Cu})_0 = 0$ to be 1. Addition of hydroxide up to $(\text{OH}/\text{Cu})_0 = 1$ gives a relative intensity of 0.3 and a further hydroxide addition up to $(\text{OH}/\text{Cu})_0 = 2$ leads to a relative intensity of 0.1.

As was already observed for the low molar mass Cu(II)–DMAP complexes, the above-mentioned observations suggest that the only EPR-detectable Cu(II)–polymer (2) complex is the species $\text{Cu(II)(ligand)}_4\text{X}_2$, irrespective of the presence of hydroxide ($\text{X} = \text{OH}^-$ or Cl^-). Other species seem to be EPR-silent and are most probably dimeric. Thus, the species $\text{Cu(II)(ligand)}_4\text{X}_2$ is present in nearly all cases (see Table 4), but it can be transformed into an EPR-silent (dimeric) species upon addition of hydroxide ions.

Reaction order in $[\text{Cu(II)}]_0$

In our study on non-polymer-bound Cu(II)–DMAP complexes [1] we reported that

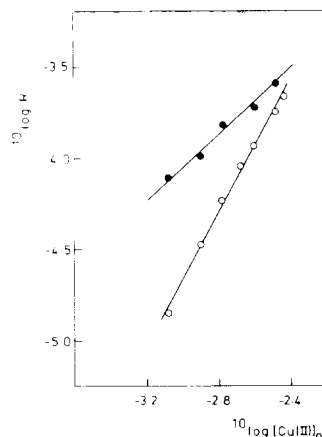


Fig. 10. $10 \log R$ versus $10 \log [\text{Cu(II)}]_0$. Standard conditions with ligand/Cu = 4 and $(\text{OH}/\text{Cu})_0 = 1$. (○) DMAP-based catalyst; (●) polymer (2)-based catalyst ($\alpha = 0.226$).

for the system with DMAP/Cu = 4 and $(\text{OH}/\text{Cu})_0 = 1$ the reaction order in $[\text{Cu(II)}]_0$ is nearly 2. In this case the reoxidation of Cu(I) was rate determining, and it was concluded that, although the catalytically most active Cu(II) complexes for the oxidation of DMP are mononuclear, dimerization of Cu(I) species is necessary for the reoxidation step. For comparison, the order in $[\text{Cu(II)}]_0$ was also determined for the copper complexes of polymer (2), naturally for the system with ligand/Cu = 4 and $(\text{OH}/\text{Cu})_0 = 1$. In Fig. 10 a plot of $10 \log R$ versus $10 \log [\text{Cu(II)}]_0$ is given, both for the low molar mass and the polymeric catalyst. For the polymeric catalyst the order in $[\text{Cu(II)}]_0$ proved to be approximately 1. One should note that in this case the oxidation of DMP is rate determining.

DISCUSSION

Structure of Cu(II)–polymer (2) complexes

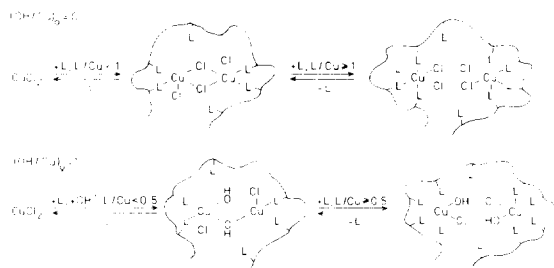
The described EPR experiments made clear that mononuclear species of the type CuN_4 are present in the catalytically active solution both in the absence and in the presence of

initially added hydroxide. Moreover in both cases the concentration of this species increased on enhancing the ligand/Cu ratio (see Figs. 8 and 9). On the other hand the species CuN_4 is transformed into an EPR-silent, probably dimeric species on addition of copper coordinating hydroxide ions (compare Fig. 8a with Fig. 9a). The same observations were made for low molar mass Cu(II)–DMAP complexes [1]. Furthermore the EPR parameters of both low molar mass and polymeric mononuclear complexes proved to be exactly the same. For the low molar mass catalyst it was found that $g_{\perp} = 2.04 \pm 0.01$, $g_{\parallel} = 2.24 \pm 0.01$ and $A_{\parallel} = 180 \pm 2$ G, completely in agreement with the values in Table 4. In addition Figs. 5 and 6 show, after a build-up of one type of species, isosbestic points, indicating a transformation from one coloured species into another upon addition of more ligands. As with the low molar mass catalyst the single-topped maxima around 620 nm are attributed to the absorption of mononuclear complexes. Usually, octahedral copper complexes show single-topped maxima [12]. This maximum increases on enhancing the ligand/Cu ratio which is in perfect agreement with our EPR results (see earlier). Moreover the absence of EPR-active species such as CuN_4 , i.e., the presence of EPR-silent (dimeric) species, is accompanied by the presence of double maxima around 800 nm in the UV spectra. Looking at Table 4 we can conclude that for $(\text{OH}/\text{Cu})_0 = 0$ and ligand/Cu < 2 all ligands are coordinated to EPR-silent (probably dimeric) species, as in those cases the EPR spectrum of CuCl_2 is observed (see Fig. 8a). EPR-active species with the formula CuN_4 and with nitrogen super-hyperfine splitting are observed for ligand/Cu > 2 (see Figs. 8c and d). When $(\text{OH}/\text{Cu})_0 = 1$, the species CuN_4 is already detectable for ligand/Cu > 1.

Summarizing we conclude that in all systems under investigation the only mononuclear copper(II)–DMAP species present in

relatively large amounts are of the type $\text{Cu(II)(ligand)}_4\text{X}_2$ where $\text{X} = \text{Cl}^-$ or OH^- or both. These mononuclear species are in equilibrium with EPR-inactive, probably dimeric, species. Addition of extra polymeric ligands yields more mononuclear CuN_4 . On the other hand, on addition of copper-coordinating hydroxide the EPR intensity of CuN_4 is reduced and the concentration of dinuclear copper complexes is believed to be enhanced. Exactly the same was concluded for the low molar mass Cu(II)–DMAP catalyst [1]. For the low molar mass catalyst an X-ray analysis proved that the DMAP ligands are coordinated to Cu(II) through the pyridine nitrogen atoms in a tetragonal geometry. The same may be assumed for our copper catalyst based on polymer (2).

An important difference between the low molar mass and polymeric complexes is the following. For the polymeric catalyst with $(\text{OH}/\text{Cu})_0 = 0$, the transformation of dinuclear into mononuclear complexes upon ligand addition, which is preceded by a build-up of dinuclear complexes out of CuCl_2 and ligands, already starts at ligand/Cu = 1 (see isosbestic point in Fig. 5). For the low molar mass catalyst this transformation started not before ligand/Cu = 2 [1]. In the presence of hydroxide ($(\text{OH}/\text{Cu})_0 = 1$) the transformations are already detectable at ligand/Cu = 0.5 for the polymeric catalyst (Fig. 6) and at ligand/Cu = 1 for the low molar mass catalyst. Moreover for the polymeric catalyst with $(\text{OH}/\text{Cu})_0 = 0$, the transformation of dinuclear into mononuclear complexes seems to be nearly completed for ligand/Cu \approx 7 (see Fig. 7). In case of the low molar mass catalyst this transformation was still incomplete even for ligand/Cu = 13 [1]. We are convinced that both points of difference between the polymeric and the low molar mass catalyst can be ascribed to the polydentate effect of the polymer (2). If one ligand becomes coordinated to Cu(II), then the coordination of subsequent ligands is facilitated due to the high local



Scheme 4

ligand concentration around Cu(II) and a smaller loss of entropy for intramolecular complexation.

In Scheme 4 the build-up of dimeric complexes and the subsequent equilibrium between dimeric and monomeric copper complexes are presented schematically for polymer ligand (**2**).

As was found for the low molar mass catalyst the UV absorption of the mononuclear complex for $(\text{OH}/\text{Cu})_0 = 1$ levels off at a lower ligand/Cu ratio than in the case of $(\text{OH}/\text{Cu})_0 = 0$. Moreover the enhancement of the concentration of the species CuN_4 is rather low for ligand/Cu > 4.

Finally we want to emphasize that the isobestic points in Figs. 5 and 6 are not very sharp. This might indicate that besides the mentioned equilibrium between dinuclear and mononuclear complexes, other processes take place in solution. This, however, is still a point of investigation. Preliminary EPR experiments indicated that in fact Cu(II) ions play a role. Moreover the isobestic point for the experiments without initial hydroxide addition looks sharper than for the experiments with $(\text{OH}/\text{Cu})_0 = 1$, indicating that hydroxide may also play a role.

Results of catalytic and kinetic experiments

As with the low molar mass Cu(II)–DMAP catalyst, it is our intention to explain the catalytic results in terms of the structure of the catalytically active species in solution.

Figure 1 shows that for $(\text{OH}/\text{Cu})_0 = 0$ as well as $(\text{OH}/\text{Cu})_0 = 1$ the catalytic activity of the solution increases strongly upon going from ligand/Cu = 0 to ligand/Cu \approx 4. Comparing Figs. 1 and 7 it becomes clear that this sharp increase in R is accompanied by a sharp increase of the concentration of the mononuclear complex $\text{Cu}(\text{II})(\text{ligand})_4\text{X}_2$. Thus, the catalytic activity seems to be primarily determined by the amount of mononuclear complex, although we cannot completely exclude the accelerating effect of the increasing basicity of the solution from ligand/Cu = 0 to higher values [4,13]. The activity of the complex is maximum for $(\text{OH}/\text{Cu})_0 = 1$ (see Fig. 3). Addition of more hydroxide reduces the overall activity of the catalyst because of a reduction of the concentration of CuN_4 and poisoning (decomposition) of the catalyst. For the low molar mass catalyst the structure of the catalytically most active species was thought to be $\text{Cu}(\text{II})(\text{DAMP})_4(\text{OH})\text{Cl}$. Correspondingly, the structure of the most active copper catalyst based on polymer (**2**) is assumed to be $\text{Cu}(\text{II})(\text{ligand})_4(\text{OH})\text{Cl}$.

From Fig. 1 we can conclude that our polymer (**2**)-based copper complexes are catalytically active without initial hydroxide addition. However, long initiation periods of the reactions are observed in these cases (see Table 3 and Fig. 2). It is likely that the basic ligands produce their own hydroxide out of small amounts of water present in the reaction mixture (see earlier). After a certain period the concentration of OH^- is large enough to start the reaction and to make the dioxygen consumption detectable. The oxidative coupling reaction produces more water, thereby facilitating the hydroxide production and enhancing the reaction rate. In this way the unusual shape of the dioxygen-consumption curves (Fig. 2b) is explained. In the case of $(\text{OH}/\text{Cu})_0 = 1$, the optimum OH/Cu ratio is already present at the beginning, and usually the rate of OH^- production is much

slower than the oxidative coupling reaction itself. Thus, in this case a normal Michaelis–Menten type of dioxygen-consumption curve is observed.

From Fig. 1 it is obvious, that for ligand/Cu ratios exceeding 4 or 5 the increasing basicity of the reaction medium has almost a minor influence on the reaction rate. In case of the low molar mass catalyst this influence was large [1]. It was stated, that in a more basic medium more phenolate anions are produced from the substrate DMP. These negatively charged substrate anions coordinated more strongly to the low molar mass copper catalyst than the uncharged DMP molecules. In case of the polymeric catalyst, however, the catalytically active sites are located in a nonpolar environment of polystyrene chain segments. Obvious for this reason the sites are less accessible for the phenolate anions.

It has already been mentioned that the optimum (OH/Cu) ratio for the polymer (2)-based catalyst was found to be unity (Fig. 3). The optimum in Fig. 3, however, is rather broad. For the low molar mass Cu(II)–DMAP catalyst this optimum is also located at (OH/Cu)₀ = 1, but it is sharp (see Fig. 3). The same was observed before, for a higher [Cu(II)] [1]. Obviously, the polymer (2)-based catalyst is more resistant to an excess of hydroxide, which may be ascribed to the polydentate effect of the polymeric catalyst. In order to minimize the effect of extra hydroxide production, reaction rates for the unbound catalyst were determined at about 20% of the total conversion.

For all reaction systems with (OH/Cu)₀ = 1 the double reciprocal plots of R^{-1} versus $[\text{DMP}]^{-1}$ yield straight lines intersecting the y -axis, indicating that Michaelis–Menten kinetics are valid.

From Table 1 we learn that, within experimental error, k_2 and K_m^{-1} are independent of [Cu(II)] for the polymer (2)-based catalyst. It is striking that the k_2 value of 0.22 s⁻¹ of the

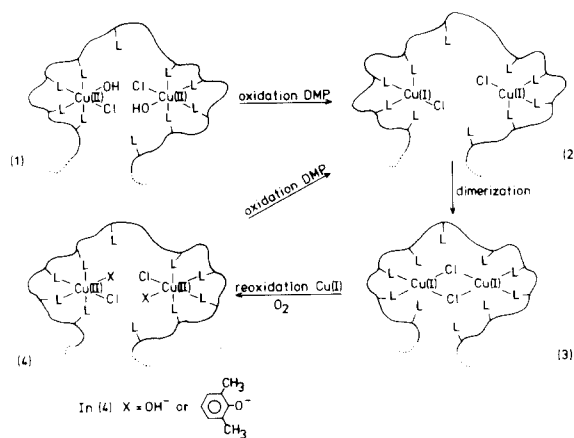
copper catalyst based on polymer (2) prepared by copolymerization of styrene and monomer (1) is higher than all k_2 values of the polymeric catalysts prepared by Verlaan et al. [4]. This might indicate that Verlaan's polymers have indeed formed some crosslinks (see Introduction) and that our method of preparation seems better. However, we cannot exclude the possibility that k_2 depends on α for $\alpha > 0.173$ (see Table 1). Such an effect of chain loading was already observed for other polymeric ligands [2,14]. In order to check this, a sample of polymer (2) with $\alpha = 0.134$ was synthesized by the copolymerization method. The value of k_2 was determined under standard conditions, with ligand/Cu = 2, [Cu(II)] = 3.32 mmol dm⁻³ and (OH/Cu)₀ = 1, and proved to equal the k_2 values of Verlaan's polymers, indeed. So, the intrinsic activity of the copper complexes based on polymer (2) depends on the chain loading α for $\alpha > 0.173$. We will investigate this phenomenon in more detail, especially for ligand/Cu = 4, and we will report our results in a forthcoming paper.

Table 1 shows that our polymer (2)-based catalyst has an extraordinary high k_2 value of 0.5–0.6 s⁻¹ for $\alpha = 0.226$ and ligand/Cu = 4, although a small part of the Cu(II) is still present in less-active dinuclear copper complexes (see Fig. 7). Even when the amount of dinuclear species is considerable (ligand/Cu = 2, see Fig. 7), k_2 is still 0.22 s⁻¹ for $\alpha = 0.226$. For comparison k_2 values of some other polymeric amine–copper catalysts for the oxidative DMP coupling are given here: Cu(II) complexes of poly(styrene-co-4-vinylpyridine) have $k_2 = 0.015$ s⁻¹ [14] and Cu(II) complexes of poly(styrene-co-*N*-vinylimidazole) have $k_2 = 0.13$ s⁻¹ [5]. The former catalytically active species proved to be dinuclear containing OH⁻ as bridging ligands between two Cu(II) nuclei [15].

Finally we want to comment on the different order in [Cu(II)]₀ for the polymer (2)-based catalyst and the low molar mass

DMAP-based catalyst (see Fig. 10). In our paper on unbound Cu(II)–DMAP complexes, for which the reoxidation of Cu(I) is rate determining, it was already concluded that the catalytically most active species for the oxidative coupling of DMP is Cu(II) (DMAP)₄Cl(OH), and that the role of Cl⁻ in this species is probably that of a bridging counterion promoting the formation of dinuclear Cu(I) complexes which are necessary for the reoxidation step. The observed second-order dependence on [Cu(II)]₀ indicates the formation of such dinuclear reoxidation complex. In case of the polymeric catalyst the Cu(I) complexes are very close to each other. Accordingly dimerization of these complexes occurs intramolecularly and no second-order dependence on [Cu(II)]₀ is observed (actually the order is approximately 1). It is very likely that this is an important reason why in the case of the polymeric catalyst the reoxidation of Cu(I) is not rate determining. It seems to us that, at least in the case of polymer (2), the explanation given by Tsuchida et al. [6], i.e., that the reoxidation of Cu(I) is enhanced with respect to the low molar mass catalyst by the nonpolar field formed by the polymer backbone, is insufficient. The promotion of the mentioned dimerization by the polymer ligand is another nice example of a polymer-chain effect. In Scheme 5 this polymer-chain effect is drawn schematically. Actually another polymer-chain effect is shown in Scheme 5. As Cu(I) can only coordinate to 4 ligands, 2 Cu–L bonds per Cu(I) must be broken in order to establish structure (3) in Scheme 5. Once the reoxidation to Cu(II) has taken place the coordination of Cu(II) by Cl⁻, X⁻ and 4 L can be restored, which, of course, is facilitated by the polydentate effect.

In drawing Scheme 5 it was assumed that incoming DMP molecules abstract hydroxide from the catalytic complexes. For this process indications have been found in our laboratory for a TMED-based Cu(II) catalyst [16] (TMED = *N,N,N',N'*-tetramethylethane-1,2-diamine).



Scheme 5

In conclusion we may say that from a structural point of view copper(II) complexes based on polymer (2) behave in the same way as a catalyst as low molar mass Cu(II)–DMAP complexes. For both types of catalysts an equilibrium between dinuclear and mononuclear Cu(II) complexes is found. In fact a similar equilibrium for other ligands has been reported by other authors [17,18]. It is concluded that for both low molar mass and polymeric complexes the mononuclear Cu(II) species are the most active ones for the oxidation of DMP. Furthermore, for both polymeric and low molar mass catalysts, dimerization of Cu(I) complexes is believed to be necessary for the reoxidation step.

The catalytic specificity of the Cu(II) complex of polymer (2)

Below the general trends shown in Table 2 will be discussed.

The fact that complexes with (OH/Cu)₀ = 1 are more specific for PPO formation than complexes without added hydroxide was observed before [14].

On enhancing the ligand/Cu ratio the basicity of the reaction medium is increased, and thus the formation of phenolate anions is favoured. In this way C–O coupling, leading

to the product PPO, is promoted [13]. Besides we should keep in mind that the concentration of the mononuclear species is relatively high when the ligand/Cu ratio is high. Thus, as was found for the low molar mass catalyst, the presence of $\text{Cu(II)(ligand)}_4\text{Cl(OH)}$ together with the presence of phenolate anions, seems favourable for PPO production. However, in the case of $(\text{OH}/\text{Cu})_0 = 1$ the specificity is only slightly enhanced when the ligand/Cu ratio is increased from 4 to higher values. This is in line with the effect on activity as shown by the curves for polymer (2) in Fig. 1.

Table 2 shows that the maximum PPO yield is about 96–97%. Exactly the same is observed in our laboratory for a TMED-based Cu(II) catalyst [16]. It is known that the amine–copper catalysts for the oxidative coupling of phenols can be destroyed by water [19]. This destruction may lead to a lowering of the catalytic specificity [20], and we feel that it is responsible for the observed limitation of the PPO yield.

Finally a higher $[\text{Cu(II)}]$ yields more PPO. On the other hand a raise in $[\text{DMP}]$ with constant $[\text{Cu(II)}]$ does not influence the specificity. A higher catalyst concentration implies a higher concentration of non-coordinated ligands, and thus a higher basicity of the reaction medium. As described above this will lead to a higher PPO production.

The initiation period in absence of added hydroxide

In the discussion of the catalytic experiments it was made plausible that in the case of $(\text{OH}/\text{Cu})_0 = 0$ hydroxide ions may be produced out of water present in the reaction medium by non-coordinated basic ligands. The initial presence of OH^- proved to be necessary in order to have low Δt values. Below we will discuss the trends shown in Table 3.

When the ligand/Cu ratio is enhanced, Δt

is reduced. A higher overall ligand concentration implies a higher concentration of non-coordinated ligands. This leads to a faster hydroxide production and thus to a shorter initiation period.

When $[\text{Cu(II)}]$ is decreased, and the ligand/Cu ratio remains the same, then the overall concentration of non-coordinated ligands is also reduced. Consequently Δt will become larger (see above).

The fact that Δt values for the catalyst based on polymer (2) exceed Δt values for comparable systems based on DMAP [1], may be explained by a difference in basicity of both ligands. Because of the electron-withdrawing character of the benzyl group, the polymeric ligand is somewhat less basic. The consequence is a slower hydroxide production and a longer initiation period Δt .

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