

Copper(II) complexes of "polystyrene-bound DMAP" : effect of chain loading on the catalytic activity in the oxidative coupling of 2,6-dimethylphenol

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COPPER(II) COMPLEXES OF “POLYSTYRENE-BOUND DMAP” *: EFFECT OF CHAIN LOADING ON THE CATALYTIC ACTIVITY IN THE OXIDATIVE COUPLING OF 2,6-DIMETHYLPHENOL **

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The effect of the degree of loading, α , of polystyrene with DMAP ligands on the catalytic activity of “polystyrene-bound DMAP”-copper catalysts in the oxidative coupling of 2,6-dimethylphenol was studied. The intrinsic activity increases upon enhancing α from 0.096 to 0.23. This increase proved to be mainly brought about by an increasing “strain” in the polymeric catalyst. An additional accelerating effect is the increase of the amount of catalytically active mononuclear complexes $\text{CuL}_4(\text{OH})\text{Cl}$ with increasing α up to $\alpha = 0.134$. This is due to a stronger polydentate effect for higher α because of the higher local ligand concentration within the polymer coils, which can be regarded as separate micro-reactors. For $\alpha > 0.23$ the interligand distance becomes too short to link adjacent ligands to the same copper ion. Consequently, some ligands have to be skipped in favour of next ones, the strain is somewhat released and the intrinsic activity slightly decreases. For $\alpha \geq 0.096$ the phenol oxidation step proved to be rate limiting. However, for very low chain loadings, e.g. $\alpha = 0.044$, the local concentration of mononuclear copper complexes within the coils becomes too low and the dimerization which is needed for the Cu(I) reoxidation becomes rate determining. The catalytic specificity proved to be independent of α under our reaction conditions.

INTRODUCTION

Copper complexes of DMAP and “polystyrene-bound DMAP” (structures (1) and (2)

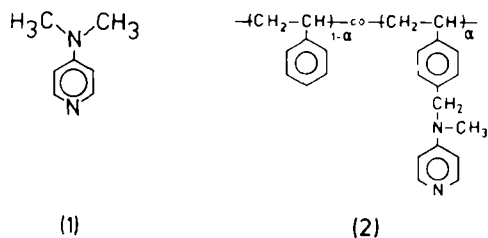
* Poly[styrene-co-4-(*N*-methyl-*N*-*p*-vinylbenzylamino)pyridine].

** Paper presented at the ESF Workshop on Reactive Polymers as Supports and Catalysts, Tirrenia, Italy, October 1–3, 1986.

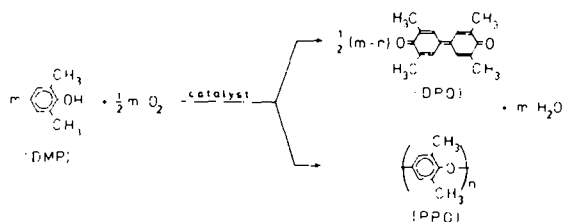
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in Scheme 1, respectively) proved to be very active and specific catalysts for the oxidative polymerization of 2,6-dimethylphenol (DMP) to polyphenyleneoxide (PPO) [1–3]. Only a minor amount of the undesired by-product diphenoquinone (DPQ) is formed, provided that the reaction conditions are suitably chosen (see Scheme 2).

In a catalytically active solution an equilibrium proved to exist between dinuclear and



Scheme 1.



Scheme 2.

mononuclear copper–DMAP complexes [2,3]. The concentration of the mononuclear species $\text{Cu(II)L}_4(\text{OH})\text{Cl}$ (where $\text{L} = \text{DMAP}$ for both (1) and (2) in Scheme 1) increases on enhancing the ratio L/Cu . A higher $\text{Cu(II)L}_4(\text{OH})\text{Cl}$ concentration yields a higher activity of the catalyst solution. Actually, for $\text{L}/\text{Cu} = 4$ and $(\text{OH}/\text{Cu})_0 = 1$ and using standard conditions the only spectroscopically detectable species is this mononuclear species. Furthermore, it was found that for the reoxidation of mononuclear Cu(I) complexes, which are formed from mononuclear Cu(II) complexes when DMP is oxidized, dimerization of these complexes is needed [2,3].

In comparing the polymer-bound Cu(II) –DMAP catalyst (Cu(II) –PS–DMAP) with its low molar mass analogue (Cu(II) –DMAP), several polymer effects were observed [3]. Extensive descriptions of polymer chain effects were given for example, by Pittman [4], Ciardelli et al. [5] and Bootsma and Challa [6]. An important polymer effect which was observed in our system was the higher catalytic activity of the polymer catalyst, for which several reasons can be given. First, the polymer chain plays an important role in the reoxidation of mononuclear Cu(I) complexes

(see above). For the low molar mass Cu(II) –DMAP complexes this reoxidation of Cu(I) to Cu(II) is rate limiting at our standard conditions, and a second-order rate dependence on $[\text{Cu(II)}]_0$ is observed. For the polymer-bound catalyst the Cu(I) dimerization, and thus the reoxidation to Cu(II) , is promoted by the high local copper concentration in the polymer coils. In addition, the rate constant for the electron transfer in the reoxidation to Cu(II) may be enhanced by the non-polar field which is created by the polymer backbone [7]. Consequently, for the polymer catalyst the Cu(I) reoxidation is no longer rate limiting and real DMP oxidation rates are measured under standard conditions. Moreover, the polymer chain has some accelerating effects on the oxidation of DMP as well. Thanks to the high local DMAP concentration in the polymer coil the stability of Cu(II) –PS–DMAP towards, for example, an excess of hydroxide is higher [2] and the coordination of one Cu(II) ion by four ligands can occur very effectively. This phenomenon is called the “polydentate effect,” and good examples of it were reported by Nishikawa and Tsuchida [8] and Challa [9]. An important consequence of the high local ligand concentration is that, for a given L/Cu ratio, the concentration of the catalytically highly active mononuclear species $\text{Cu(II)L}_4(\text{OH})\text{Cl}$ is higher in the case of Cu(II) –PS–DMAP and thus a higher activity in the DMP oxidation may be expected (see above). As an illustration the absorbance of mononuclear complexes, $A_{\text{Cu(II)L}_4(\text{OH})\text{Cl}}$, is drawn in Fig. 1 as a function of L/Cu for both polymer-bound and unbound copper–DMAP complexes. Most catalytic experiments were carried out at $\text{L}/\text{Cu} = 4$. At this L/Cu ratio a difference in the concentration of the active species for the DMP oxidation is obvious, but it can hardly account for the large difference in activity (measured as O_2 uptake) observed at $\text{L}/\text{Cu} = 4$ (see also Fig. 1).

Challa and coworkers have reported

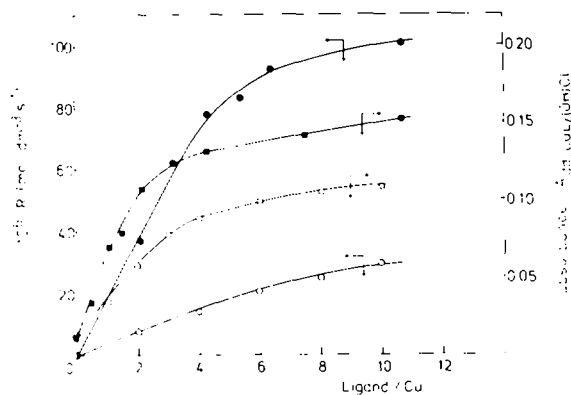
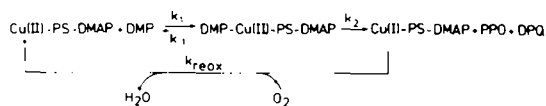


Fig. 1. Dioxygen consumption rate R as a function of L/Cu for PS-DMAP (●, $\alpha = 0.251$) and DMAP (○) and the visible absorbance of the mononuclear complex $A_{Cu(II)(OH)Cl}$ as a function of L/Cu for PS-DMAP (■, $\alpha = 0.251$, $\lambda_{max} = 636$ nm) and DMAP (□, $\lambda_{max} = 630$ nm). Standard conditions with $(OH/Cu)_0 = 1$ (■ and □ without DMP).

another, very interesting polymer chain effect for several polymer-copper catalysts in the oxidative coupling of 2,6-disubstituted phenols, viz., for copper complexes based on polymer-bound dimethylamines, polymer-bound pyridines and polymer-bound imidazoles [10,11]. This chain effect proved to accelerate the DMP oxidation step by strain in the intermediate chain segments linking neighbouring amine ligands coordinated in the same copper complex. The observed acceleration proved to increase with the chain loading, α . In our previous study on polymeric copper-DMAP complexes a similar effect was observed [2].

Reconsidering Fig. 1 it seems that the major factors determining the high activity of the polymer catalyst with respect to its low molar mass analogue must originate from the acceleration of the Cu(I) reoxidation and from the above-mentioned strain in the polymeric catalyst.

Usually, with Cu(II)-PS-DMAP catalysts, Michaelis-Menten kinetics in terms of the substrate DMP are obeyed in the oxidative



Scheme 3.

polymerization [1,2] (see Scheme 3). Thus, Lineweaver-Burk plots of R^{-1} versus $[DMP]^{-1}$ yield straight lines intersecting the y -axis according to the equation:

$$\frac{1}{R} = \frac{1}{k_2[Cu(II)]_0} + \frac{K_m}{k_2[Cu(II)]_0[DMP]_0} \quad (1)$$

In eqn. (1), K_m is the Michaelis constant ($= (k_{-1} + k_2)/k_1$), k_2 is the rate constant of the rate-limiting oxidation of DMP and $k_2[Cu(II)]_0 \equiv R_{max}$ is the dioxygen consumption rate at infinite DMP concentration.

In this paper, a detailed investigation of the “ α -effect” in catalysis using Cu(II)-PS-DMAP is reported. For this purpose, R_{max} has been determined as a function of the chain loading, α . Supporting UV/Vis experiments were carried out in order to help to explain the catalytic results obtained.

EXPERIMENTAL

Materials

For catalytic and spectroscopic experiments, 1,2-dichlorobenzene, KOH and $CuCl_2 \cdot 2H_2O$ were from Merck and analytically pure. The copper salt and the hydroxide 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.

For the syntheses described below, all chemicals were chemically pure and used without further purification.

Synthesis of 4-(*N*-methyl-*N*-*p*-vinylbenzylamino)pyridine (3)

Monomer (3) was synthesized mainly as described before [2], viz., by a slight modification of the method of Tomoi et al. [12]. Improvements are described below. These concern the chloromethylation of 2-phenylethyl bromide and the synthesis of 4-(*N*-methylamino)pyridine.

An amount of 178.4 g (0.96 mol) of 2-phenylethyl bromide was chloromethylated by the method of Galeazzi [13]. 350 ml of 1,2-dichloroethane was added to dilute the reaction mixture. The reaction was carried out at 30 °C and the conversion was followed by recording the IR absorption of CH₂Cl at 675 cm⁻¹. After 7 days the reaction was stopped, and 114.5 g (0.49 mol) of pure *p*-(2-bromoethyl) benzyl chloride was isolated from the *o*, *p*-product mixture as described by Kondo et al. [14] (Yield: 51%; m.p. 49.5–52 °C, lit. [14] m.p. 48–50 °C). Subsequently *p*-(2-bromoethyl)benzyl chloride was transformed into *p*-chloromethylstyrene as described previously [14].

4-(*N*-Methylamino)pyridine was synthesized in aqueous solution as described by Wibaut and Broekman [15]. 4-Chloropyridine hydrochloride was used instead of 4-chloropyridine and the reaction was carried out under N₂ in sealed Carius tubes (155 °C; 12 h). After working up the product it was treated with activated charcoal and recrystallized from diethyl ether. The yield was 70%, m.p. 124–126 °C (lit [15] m.p. 124.5–125 °C).

The reaction of *p*-chloromethylstyrene with the sodium salt of 4-(*N*-methylamino)pyridine as well as the purification of monomer (3) were carried out as described previously [2], and pure monomer (3) was obtained in 90% yield.

Synthesis and characterization of polystyrene-bound DMAP (2)

Linear polystyrene-bound DMAP (2) was prepared as described before by radical

copolymerization of styrene and 4-(*N*-methyl-*N*-*p*-vinylbenzylamino)pyridine (3) using AIBN as an initiator [2]. The polymers were precipitated in petroleum-ether (40/60)/diethyl ether = 2/1 (v/v) and reprecipitated twice from chloroform in petroleum-ether (40/60)/diethyl ether = 2/1 (v/v).

Number-average molar masses, \overline{M}_n , were determined in chloroform with a Knauer membrane osmometer. The degree of functionalization (α) of the synthesized polymers was determined by elemental analysis. For details concerning the polymerizations and the characterizations of the polymers the reader is referred to the Results Section (below and Table 1).

Oxidative coupling

The standard conditions for oxidative coupling were: $T = 298.2$ K, $[\text{Cu(II)}] = 8.3 \times 10^{-4}$ mol dm⁻³, $[\text{DMP}] = 0.06$ mol dm⁻³, $P_{\text{O}_2} = 101.3$ kPa, total reaction volume = 0.015 dm³, solvent mixture 1,2-dichlorobenzene/methanol = 13/2 (v/v). The polymeric catalyst was prepared *in situ* by dissolving the polymer ligand (2) in 1,2-dichlorobenzene and adding methanolic solutions of CuCl₂ · 2H₂O and KOH in the optimum ratio of $(\text{OH}/\text{Cu})_0 = 1$ [2]. The reaction vessel was connected with an automatic gas burette with pure dioxygen [16]. After saturating the catalyst solution with dioxygen the reaction 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 mixture were diluted with solvent mixture. The concentration of the only and undesired by-product diphenoquinone (DPQ) in these diluted mixtures was 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.

Spectroscopic analysis of the polymeric Cu(II) complexes

UV/Vis spectra of solutions of the polymeric Cu(II) complexes were recorded on a Pye Unicam SP 8-200 UV/Vis spectrophotometer at 298.2 K.

RESULTS

Polymerizations

In Table 1 data concerning the syntheses and characterizations of the PS-DMAP ligands used in this paper are given.

The polymers with $\alpha = 0.222$ and $\alpha = 0.237$ were obtained from the same reaction mix-

ture. The polymerization was started and after 1 h half of the reaction mixture was precipitated under a nitrogen atmosphere. The conversion of the polymerization proved to be not much higher than 5% (see Table 1). The chain loading of the purified sample was $\alpha = 0.237$. The remaining half of the initial polymerization mixture was allowed to polymerize for another 64 h, resulting in a polymer with $\alpha = 0.222$. In this case the conversion was at least 60%. The results of these experiments may indicate that a rather random copolymer is formed, even for high conversions of the polymerizations. No attempts were undertaken to determine the exact reactivity ratios of styrene and monomer (3).

Catalysis and specificity of PPO formation

For all polymer ligands listed in Table 1 the dioxygen consumption rate R was determined as a function of the DMP concentration. Standard conditions were used with $L/Cu = 4$ and $(OH/Cu)_0 = 1$. Lineweaver-Burk plots of R^{-1} versus $[DMP]^{-1}$ for these polymer catalysts yielded straight lines intersecting the y -axis, indicating that for all investigated chain loadings α , Michaelis-Menten kinetics in DMP are valid. For some α values the plots of R^{-1} versus $[DMP]^{-1}$ are shown in Fig. 2.

For $\alpha \geq 0.096$ an increase of P_{O_2} from 101.3 kPa to 131.7 kPa did not affect R within experimental error, indicating that under the conditions which were used to construct Fig. 2 DMP oxidation rates are measured rather than Cu(I) reoxidation rates. This was also observed by Verlaan et al. [1] for an almost identical system with $L/Cu = 2$ for $0.056 \leq \alpha \leq 0.173$. For our copolymer with $\alpha = 0.044$, however, an increase of P_{O_2} by a factor 1.3 resulted in a 17% increase of R , which is far beyond experimental error. More attention to this point will be given below.

From the intercepts of all constructed Lineweaver-Burk plots, R_{\max} was determined.

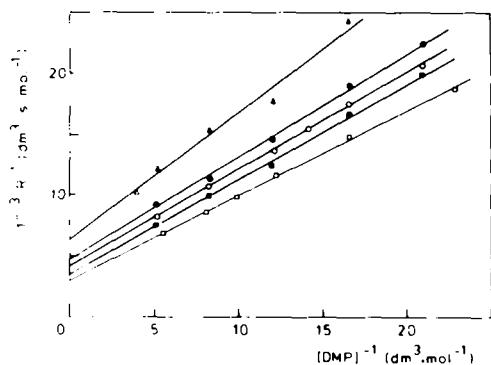


Fig. 2. Lineweaver-Burk plots of R^{-1} versus $[DMP]^{-1}$ for some PS-DMAP ligands. Standard conditions with $L/Cu = 4$ and $(OH/Cu)_0 = 1$. (Δ) $\alpha = 0.044$; (\bullet) $\alpha = 0.096$; (\circ) $\alpha = 0.134$; (\blacksquare) $\alpha = 0.187$; (\square) $\alpha = 0.251$.

TABLE 1

Data on the synthesis and characterization of polymers (2) with varying chain loading α . The polymerizations were carried out under N_2 at 75–80°C

Amount of monomer (3) (g)	Amount of styrene (g)	Mol % of AIBN ^a	Amount of toluene (g)	Polymerization time (h)	Yield of polymer (2) (g)	Chain loading, α	\overline{M}_n (g mol ⁻¹)
3.00	35.60	1.0	30.0	40	22.7	0.044	2.2×10^4
0.65	3.02	1.0	11.0	40	2.2	0.096	4.0×10^4
0.91	2.59	1.0	10.5	40	2.1	0.134	3.3×10^4
1.21	2.39	1.0	10.8	40	2.1	0.187	4.3×10^4
2.16	3.80	1.0	17.4	65	3.6	0.220	3.6×10^4
1.03	1.91	1.0	8.7	65	1.8	0.222	3.3×10^4
1.03	1.91	1.0	8.7	1	0.09	0.237	?
2.00	3.33	1.0	17.0	65	3.2	0.224	3.3×10^4
10.30	18.10	^b	22.4	65	2.0 ^c	0.233	9.4×10^4
5.28	7.34	1.0	38.1	40	8.9	0.251	4.0×10^4
1.73	2.42	1.0	13.0	40	2.4	0.251	6.4×10^4
1.61	2.70	1.0	13.0	40	1.4	0.259	4.4×10^4
2.36	2.82	1.0	13.0	40	3.0	0.283	5.6×10^4
19.33	23.54	0.3	39.0	65	27.2	0.288	12.4×10^4
7.25	6.60	0.33	34.8	65	7.6	0.357	5.9×10^4

^a Based on total monomer.

^b 4.8 g of silica-bound radical initiator (synthesized according to Fery et al. [17] on Aerosil 200 V, Degussa) was used containing ca. 0.02 mmol initiator/g silica.

^c Unbound polymer (2) produced during the grafting procedure.

In Fig. 3, R_{\max} is drawn as a function of the chain loading, α . It is obvious that an optimum intrinsic activity is achieved for $\alpha = 0.23(\pm)0.03$.

In Table 2, the percentage of DMP that is transformed into PPO (after 100% reaction

conversion) is given for several values of α . It is clear that the specificity of the polymer-bound DMAP-copper catalysts is not influenced by the chain loading, and only slightly by the L/Cu ratio.

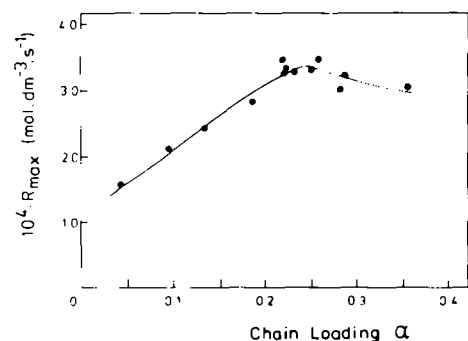


Fig. 3. R_{\max} , derived from Lineweaver–Burk plots like those drawn in Fig. 2, versus the chain loading α . Standard conditions with L/Cu = 4 and (OH/Cu)₀ = 1.

TABLE 2

Catalytic specificity determined at full conversion of the complexes Cu(II)–PS–DMAP with varying chain loading α . Standard conditions with (OH/Cu)₀ = 1

Chain loading, α	% PPO for L/Cu = 4	% PPO for L/Cu = 10
0.044	87	92
0.096	89	92
0.134	89	92
0.187	88	92
0.251	88	92
0.283	88	92
0.288	86	93
0.357	87	91

Reaction order with respect to copper

Relevant for the discussion of the α -effect is the following. For the low molar mass catalyst it was found that at standard conditions the Cu(I) reoxidation is second order with respect to copper [3]. For this system at standard conditions an increase in P_{O_2} leads to a significant increase in R . On the contrary, recent experiments have convinced us that DMP oxidation rates are first order with respect to copper. This was found by determining the order with respect to copper within the polymer coils at standard conditions for PS-DMAP with $\alpha = 0.251$ [18]. The number of polymer coils was kept constant and the amount of copper ions per coil was varied. However, if the amount of copper ions within a coil became too small, i.e., if the local copper concentration within the coils became too small, then a second-order rate dependence on copper was found and the Cu(I) reoxidation again proved to be rate limiting! So, for PS-DMAP with $\alpha = 0.044$ a significant dioxygen pressure dependence of R is observed (see earlier), which was absent for $\alpha \geq 0.096$, where pure DMP oxidation rates are measured. In this respect it is important to note that, for the copper amounts for which a second-order rate dependence within the coil with $\alpha = 0.251$ is observed, the average number of Cu(II) ions per polymer coil is still 3–5. Even for the low molar mass PS-DMAP with $\alpha = 0.044$ and standard conditions 2–3 Cu(II) ions are present per coil.

UV/Vis-spectroscopic study of complex structures in solution

UV/Vis spectra may give an indication of the composition of the complexes in solution. Hence, spectra were recorded of solutions of copper complexes based on polymer (2) with varying L/Cu values.

For both the low molar mass Cu(II)-DMAP catalyst [3] and the polymeric Cu(II)-

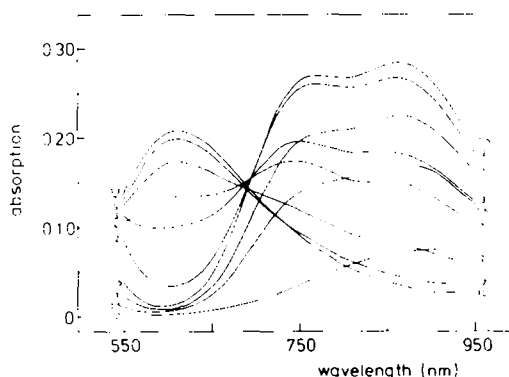


Fig. 4. d-d Absorption spectra for various L/Cu values for PS-DMAP with $\alpha = 0.357$. Standard conditions. No hydroxide and DMP were added. L/Cu values are indicated in figure.

PS-DMAP catalyst with $\alpha = 0.251$ [2] the d-d absorption spectra were found to be located in the visible region. In Fig. 4 the d-d absorption spectra for the polymeric Cu(II)-PS-DMAP complex with $\alpha = 0.357$ are drawn for $0 \leq L/Cu \leq 10$. In this case no hydroxide was added. Double maxima around 800 nm are observed for $L/Cu \leq 4$ as for the polymer ligand with $\alpha = 0.251$ [2]. For our polymeric ligand with $\alpha = 0.044$, however, double maxima around 800 nm are observed for $L/Cu \leq 6$ as for the low molar mass catalyst [3]. A detailed study has taught that these double maxima can be attributed to EPR-silent complexes, probably dinuclear or polynuclear Cu(II)-DMAP species [2,3]. For $\alpha = 0.357$ and $(OH/Cu)_0 = 0$ an isosbestic point is observed for $L/Cu \geq 1.5$, suggesting that for these values of L/Cu one "coloured" species, namely a di- or polynuclear species with $\lambda_{max} \approx 800$ nm, is transformed into another coloured species with $\lambda_{max} \approx 630$ nm. In our previous work we could prove that the single-topped absorptions around 630 nm can be ascribed to mononuclear copper complexes with the formula CuL_4Cl_2 [2,3]. For the low molar mass catalyst an isosbestic point was found for $L/Cu \geq 2$.

In Fig. 5, the d-d absorption spectra for the polymer ligand with $\alpha = 0.357$ and

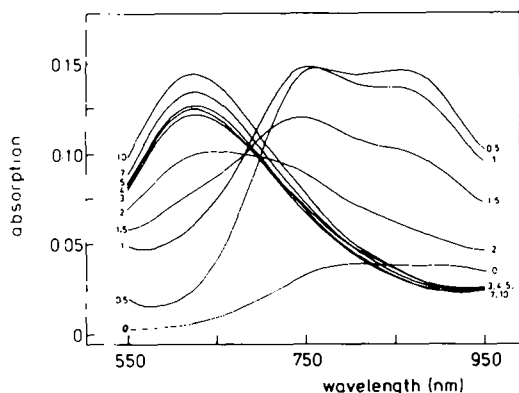


Fig. 5. d-d Absorption spectra for various L/Cu values for PS-DMAP with $\alpha = 0.357$. Standard conditions with $(OH/Cu)_0 = 1$. No DMP was added. L/Cu values are indicated in figure.

$(OH/Cu)_0 = 1$ are drawn for various values of L/Cu ($0 \leq L/Cu \leq 10$). In this case the transition of di- or polynuclear into mononuclear $Cu(II)$ -DMAP complexes already takes place for $L/Cu \geq 1$. Dinuclear complexes are present in reasonable amounts only for $L/Cu \leq 2.0$ (≤ 3 for $\alpha = 0.044$). In this case the single absorption maxima around 630 nm are attributed to the mononuclear species $CuL_4(OH)Cl$ [2,3].

From the above it is clear that in the presence of hydroxide the dinuclear $Cu(II)$ -DMAP complexes have already ceased to exist at lower L/Cu values than in the absence of hydroxide. Moreover, in the presence of hydroxide the isosbestic point becomes less well defined for higher L/Cu values for which dinuclear complexes are no longer present in the solution (see Fig. 5). Both effects were reported before [2,3]. They can be explained by assuming that $Cu(II)$ is partly present in polynuclear hydroxide-bridged $Cu(II)$ species: $Cu[(OH)_2Cu]_n$. It is known that such copper compounds can be readily formed in solvents other than water [19]. As long as dinuclear complexes exist in solution an increase of L/Cu causes a transformation of dinuclear complexes into mononuclear ones and the isosbestic point is sharp.

However, when the dinuclear complexes are exhausted the observed increase of $[CuL_4(OH)Cl]$ with the increasing L/Cu ratio must be brought about by taking away copper ions from the spectroscopically undetectable polynuclear copper compounds, and an isosbestic point can no longer be observed. The consequence of the existence of such compounds in the reaction mixture is a high effective value of L/Cu , as part of the copper ions is poorly accessible for the offered DMAP ligands. Consequently, for comparable $(L/Cu)_0$ the equilibrium between di- and mononuclear $Cu(II)$ -DMAP complexes is shifted towards the mononuclear complexes in case of added hydroxide. As an illustration the following may serve: for $\alpha = 0.357$ with standard conditions, $(L/Cu)_0 = 1.5$ and $(OH/Cu)_0 = 2$, only mononuclear complexes are present in solution, whereas Figs. 4 and 5 clearly indicate the presence of dinuclear complexes for $(L/Cu)_0 = 1.5$ for $(OH/Cu)_0 = 0$ and 1, respectively.

In Fig. 6, the UV/Vis absorption of the mononuclear complexes $CuL_4(OH)Cl$ has been plotted as a function of L/Cu for $\alpha = 0.044$, $\alpha = 0.251$ and $\alpha = 0.357$. For comparison the curve for the low molar mass catalyst

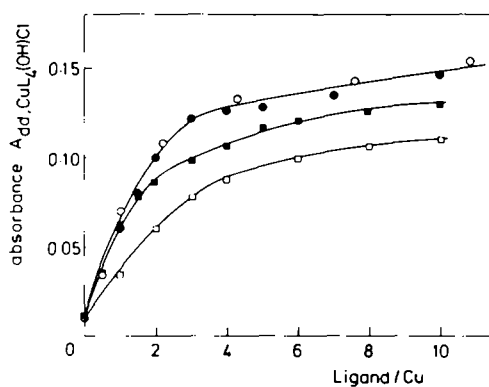


Fig. 6. Visible absorbance of mononuclear complexes, $A_{d-d, CuL_4(OH)Cl}$, as a function of L/Cu . Standard conditions with $(OH/Cu)_0 = 1$. No DMP was added. (□) Low molar mass DMAP; (■) PS-DMAP, $\alpha = 0.044$; (●) PS-DMAP, $\alpha = 0.357$; (○) PS-DMAP, $\alpha = 0.251$. Values of λ_{max} are given in Table 3.

TABLE 3

Absorption of the mononuclear complex $\text{CuL}_4(\text{OH})\text{Cl}$ around 630 nm for DMAP and PS-DMAP with different chain loadings α . Ligands marked with * have been prepared by Verlaan et al. [1] by reaction of the sodium salt of 4-(*N*-methylamino)pyridine with partially chloromethylated polystyrene. Standard conditions with $\text{L}/\text{Cu} = 4$ and $(\text{OH}/\text{Cu})_0 = 1$ and without DMP

Chain loading α	λ_{max} (nm)	$A_{\text{CuL}_4(\text{OH})\text{Cl}}$
DMAP	630	0.088
0.044	630	0.105
0.056 *	630	0.107
0.134	630	0.124
0.173 *	630	0.119
0.187	630	0.124
0.220	626	0.120
0.251	636	0.126
0.283	632	0.120
0.357	635	0.125

is given as well. According to Fig. 6 it seems as if the building up of mononuclear $\text{Cu}(\text{II})$ DMAP complexes occurs less easily for low chain loadings α . The polydentate effect (see Introduction) seems to be less pronounced in that case. For the low molar mass ligand, of course, no polydentate effect exists at all.

In Table 3, the wavelength and the absorption of the mononuclear complexes $\text{CuL}_4(\text{OH})\text{Cl}$ is given for DMAP and PS DMAP with differing chain loadings α . The conditions under which $A_{\text{CuL}_4(\text{OH})\text{Cl}}$ was measured conform to those under which the Lineweaver-Burk plots of Fig. 2 were measured, i.e., standard conditions with $\text{L}/\text{Cu} = 4$ and $(\text{OH}/\text{Cu})_0 = 1$. No DMP was added. The two PS DMAP ligands marked with superscript asterisks in Table 3 were prepared by Verlaan et al. [1] by reaction of the sodium salt of 4-(*N*-methylamino)pyridine with partially chloromethylated polystyrene.

DISCUSSION

Looking for an explanation of the observed effect of chain loading, one must keep in mind that for the polymer ligand with $\alpha = 0.044$ no real DMP oxidation rates are measured (see earlier). The $\text{Cu}(\text{I})$ reoxidation is rate determining, and a fair comparison with the polymers with $\alpha \geq 0.096$ is impossible. The reason for this is the following. For low chain loadings the distance between the copper ions along the chain is large and the local copper concentration within the coils is relatively low. Accordingly, the dimerization of mononuclear $\text{Cu}(\text{I})$ DMAP complexes, an inevitable step in the $\text{Cu}(\text{I})$ reoxidation [2,3], is retarded and the reoxidation of $\text{Cu}(\text{I})$ becomes rate determining. Exactly the same effect occurs in case of high chain loadings when the amount of copper ions per polymer coil is relatively low. This situation may arise, for example, for low values of $[\text{Cu}(\text{II})]_0$, when the order with respect to copper within a polymer coil is determined (see earlier).

For $\alpha \geq 0.096$, however, we found that real phenol oxidation rates are measured. In fact, perfect linear relationships between R^{-1} and $[\text{DMP}]^{-1}$ are observed (Fig. 2), pointing to Michaelis-Menten kinetics in terms of the substrate.

Now let us consider the spectroscopic results. R_{max} was determined at standard conditions with $\text{L}/\text{Cu} = 4$ and $(\text{OH}/\text{Cu})_0 = 1$. For polymer ligands listed in Table 1 with $\text{L}/\text{Cu} = 4$ and $(\text{OH}/\text{Cu})_0 = 1$ the only spectroscopically detectable $\text{Cu}(\text{II})$ DMAP complexes present in solution at the moment of DMP addition are the mononuclear species $\text{CuL}_4(\text{OH})\text{Cl}$. From our earlier work we know that a higher initial concentration of $\text{CuL}_4(\text{OH})\text{Cl}$ leads to a higher activity of the catalyst solution [2,3]. Table 3 shows that for $\text{L}/\text{Cu} = 4$ and $(\text{OH}/\text{Cu})_0 = 1$ the amount of $\text{CuL}_4(\text{OH})\text{Cl}$ increases with α for $\alpha < 0.134$ and levels off for $\alpha \geq 0.134$. This increase can be explained by the polydentate effect, which

is also demonstrated in Fig. 6. A higher chain loading implies a higher local ligand concentration in the polymer coil. Consequently, for a fixed value of L/Cu the coordination of $Cu(II)$ by four DMAP ligands occurs to a larger extent for higher values of α . The large difference between $Cu(II)$ -PS-DMAP and the low molar mass catalyst is striking and understandable from this point of view. From the results in Table 3 and Fig. 3 it is obvious that the relatively small increase of the amount of $CuL_4(OH)Cl$ with α cannot account for the rather strong increase of R_{max} . Moreover, for $\alpha \geq 0.134$ a significant further enhancement of R_{max} with α is observed while the amount of $CuL_4(OH)Cl$ remains constant within experimental error.

For $\alpha \geq 0.096$ the increase of R_{max} with α implies an increase of the DMP oxidation rate. As was mentioned in the Introduction, the strain in the polymeric catalyst may play an important role in the intrinsic activity of the catalyst [9–11]. A similar effect is well known in enzyme catalysis [20] and indicated by the term "entatic state" [21]. The idea is that for an entatic catalyst the activation free energy is reduced relative to a normal catalyst as a result of the strain.

Table 4 shows that, within experimental error, R_{max} is not influenced by the molar mass of the polydentate for a constant chain loading α . An increase of \bar{M}_n with constant α implies a reduction of the number of polymer

coils (and, as a consequence, an increase of the number of copper complexes per coil), while the intermediate chain length between successive DMAP ligands remains the same. On the other hand, an increase of α with (practically) constant \bar{M}_n implies a reduction of the interligand distance, while the number of polymer coils decreases as well. As an increase of α changes the catalytic activity while an increase of \bar{M}_n does not influence R_{max} , it can be concluded that the increase in catalytic activity is determined by the decreasing intermediate chain length between successive DMAP ligands coordinated in the same copper complex and not by the higher total number of copper complexes within one polymer coil for increasing α . In going from $\alpha = 0.096$ to $\alpha = 0.23$ the intermediate chain lengths become shorter, the strain in the catalyst increases and the rate of electron transfer from the substrate to $Cu(II)$ is enhanced. Challa and coworkers [10,11] found that for copper complexes of polystyrene-bound dimethylamines the increase of k_2 with α is governed by an increase of activation entropy ΔS^\ddagger with α which overcompensates for the retarding effect of a simultaneously increasing ΔH^\ddagger . This was explained in terms of an increasing number of possible conformations of the intermediate chain segments in the transition state between the $Cu(II)$ and the $Cu(I)$ complexes. For high values of α the intermediate chain segments are more strained, and therefore the number of chain conformations increases relatively more strongly when going from the octahedral $Cu(II)$ to the transition state. After the electron transfer tetrahedrally based $Cu(I)$ complexes will occur.

The explanation given above was supported by chain statistical calculations and measuring heats of complexation of $Cu(II)$ with polymers with varying α . It seems that the above-mentioned explanation is also valid for the observed effect of chain loading for our catalyst system. An effect of intermediate

TABLE 4

R_{max} at standard conditions with $L/Cu = 4$ and $(OH/Cu)_0 = 1$ for PS-DMAP- $Cu(II)$ with comparable α but differing \bar{M}_n (values derived from Table 1 and Fig. 3).

α	\bar{M}_n ($g\ mol^{-1}$)	R_{max} ($mol\ dm^{-3}\ s^{-1}$)
0.224	3.3×10^4	3.32×10^{-4}
0.233	9.4×10^4	3.29×10^{-4}
0.283	5.6×10^4	3.03×10^{-4}
0.288	12.4×10^4	3.24×10^{-4}

segment length on metal complexation was also reported for poly(amido-amines) by Barbucci et al. [22].

When the intermediate chain length between neighbouring DMAP ligands becomes too short, i.e., for $\alpha \geq 0.23$, then adjacent ligands can no longer coordinate to the same copper ion. Consequently, one ligand has to be skipped in favour of the next one, although from an entropic point of view coordination of an adjacent ligand would be more favourable. Consequently, the strain in the polymer catalyst is lower than one would expect, the accelerating factor vanishes and R_{\max} slightly decreases. In fact, the skipping of ligands can be interpreted as a lowering of the "effective" chain loading. The skipped ligands can coordinate to Cu(II) ions attached to another region of the polymer backbone, which can be considered as a kind of crosslinking. This also may have a small retarding effect on R_{\max} .

Table 2 shows that the catalytic specificity of the Cu(II) PS-DMAP catalysts is, within experimental error, independent of the chain loading. This implies that the macromolecular chain itself does not influence the catalytic specificity, which was also observed for the oxidative coupling of DMP by copper complexes of poly(styrene-co-4-vinylpyridine) [16]. Moreover, our earlier work made clear that, in spite of a differing catalytic activity for Cu(II) PS-DMAP and its low molar mass analogue, the specificity of both types of catalysts is exactly the same under comparable reaction conditions [2]. So, it seems plausible that product formation by coupling of oxidized DMP does not take place in the catalyst but in solution.

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