Investigation and immobilization of the copper complex of poly[N-(2-ethoxycarbonyl)ethyl]iminotrimethylene] as a catalyst for the oxidative coupling of 2,6-dimethylphenol

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INVESTIGATION AND IMMOBILIZATION OF THE COPPER COMPLEX OF POLY[N-(2-ETHOXYCARBONYLETHYL)IMINOTRIMETHYLENE] AS A CATALYST FOR THE OXIDATIVE COUPLING OF 2,6-DIMETHYLPHENOL

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Summary

The copper complex of poly[N-2-ethoxycarbonylethyl]iminotrimethylene] proved to be an interesting catalyst for the oxidative coupling of 2,6-dimethylphenol. Even without the addition of hydroxyl ions, necessary for most other known catalysts, its activity was high. To facilitate separation of catalyst and reaction products, the catalyst was immobilized by simple adsorption on hydrophilic silica. Adsorption experiments showed that total adsorption of the catalyst was possible, but catalytic experiments pointed to an inherent significant loss of catalytic activity after adsorption. This deactivation could be explained by assuming that no active copper complexes can be formed in the adsorption trains. The activity of the immobilized catalysts proved to be independent of their molar mass, which is in accord with the adsorption theory of Scheutjens and Fleer. For both unbound and immobilized catalysts, the Michaelis-Menten type of reaction kinetics was observed. Re-use of the catalyst was unsuccessful due to hydrolysis of the ester groups of the polymer ligand. Efforts to improve the hydrolytic stability by substituting t-butyl ester groups for the ethyl ester groups had the expected result. However, re-use was still unsuccessful because of weaker adsorption, probably due to a shielding of the ester carbonyl groups by the bulky t-butyl groups.

Introduction

In 1959 Hay discovered the oxidative coupling of 2,6-dimethylphenol (DMP) to be an excellent approach to the formation of poly-2,6-dimethyl-1,4-phenyleneoxide (PPO) [1]. Diphenoquinone (DPQ = 4-(3,5-dimethyl-

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4-oxo-2,5-cyclohexadien-1-ylidene)-2,6-dimethyl-2,5-cyclohexadien-1-one), the C—C coupled byproduct of the reaction, is not of great commercial value. The C—O coupled product PPO, however, is a very serviceable engineering plastic with outstanding properties [2, 3] (Scheme 1):

Scheme 1.

Since then, many efforts have been made to develop suitable catalysts for this process. Catalysts that suppress DPQ formation are of particular industrial importance.

It is well known that one of the best catalysts for the oxidative coupling of phenols is the copper complex of *N,N,N',N'*-tetramethylethylenediamine (TMED) [4-7]. This catalyst is very active and the specificity for PPO formation is rather good [2, 8]. Not only TMED itself, but also TMED-like structures, are often used as catalysts for the oxidative coupling [9-11]. In this study we applied poly[*N*-(2-ethoxycarbonyl)ethyliminotrimethylene] [12] and poly[*N*-(2-*t*-butoxycarbonyl)ethyliminotrimethylene] as polymeric copper ligands ((1) and (2) respectively).

Although resemblance to the TMED structure is not complete, we found copper complexes of (1) to be suitable catalysts for the above-mentioned PPO formation.

In general the kinetics of oxidative coupling of phenols with polymeric copper catalysts can be described by the Michaelis-Menten concept for enzyme catalysis [11, 13] (Scheme 2):

Scheme 2.

In Scheme 2, E and E* represent the Cu(II) and Cu(I) complexes respectively, S the substrate (DMP) and P the product (PPO and/or DPQ). Normally $k_2 \ll k_{\text{reox}}$, and the step of k_2 is rate-determining in the redox cycle. From the steady-state kinetics of the reaction it can be derived that:

$$\frac{1}{R_0} = \frac{1}{k_2[E]_0} + \frac{K_m}{k_2[E]_0[S]_0} \quad (1)$$

where R_0 is the initial dioxygen consumption rate in $\text{mol O}_2 \text{ dm}^{-3} \text{ s}^{-1}$. $[E]_0$ and $[S]_0$ are the initial concentrations of copper salt and DMP, respectively, and $K_m = (k_{-1} + k_2)/k_1$ is the Michaelis-Menten constant in mol dm^{-3} . The value of $k_2[E]_0$ is called R_{max} , the reaction rate at infinite substrate concentration. As shown by eqn. (1), k_2 and K_m (and of course $k_2[E]_0$) can be derived from double reciprocal plots of reaction rate *versus* substrate concentration, so-called Lineweaver-Burk plots, since $[E]_0$ is known.

A great disadvantage of homogeneous catalysis is the laborious and time-consuming process of separation of catalyst and products. Sometimes separation even is impossible. Verlaan *et al.* [14 - 16] solved this problem by attaching one chain end of a linear macromolecular catalyst to non-porous silica. This grafting on the silica surface, however, is very laborious. Another way to immobilize macromolecular catalysts is a simple adsorption process, as recently described by Bootsma *et al.* [17].

In this study we determined the optimum conditions for the catalyst based on polymer (1) and checked whether a Michaelis-Menten type of reaction scheme is valid. Further, we immobilized the catalyst by adsorption on silica and determined the effect on catalytic activity. The possibility of re-use of the immobilized copper complexes of (1) and (2) was also investigated, although this was not our main goal.

Experimental

Materials

1,2-Dichlorobenzene and the copper salt $\text{CuCl}_2 \cdot 2 \text{ H}_2\text{O}$ were obtained from Merck and analytically pure. Methanol was of Uvasol quality from Merck. 2,6-Dimethylphenol (DMP) was from Aldrich and was purified by recrystallization from n-hexane. The non-porous hydrophilic silica used was Aerosil 380 V with a specific surface area of $380 \pm 30 \text{ m}^2 \text{ g}^{-1}$ (containing $2.0 - 3.3 \times 10^{18} \text{ SiOH groups m}^{-2}$ according to the manufacturer), and was kindly provided by Degussa AG. It was dried for several days in vacuum at 95°C , and used without further purification. All polymers used in this study were prepared in the Laboratory of Organic Chemistry in Ghent.

Synthesis of the monomers

The azetidine monomers were synthesized according to the reaction scheme proposed by Wadsworth [18].

Monomer (1) ($R = \text{Et}$) has been described earlier [12]; Monomer (2) ($R = t\text{-Bt}$) was prepared as follows: to 0.31 mol (23.28 g; 23.8 ml) of 3-amino-1-propanol 0.78 mol (100 g) of *t*-butylacrylate was added and the mixture was heated at 110 °C for 2 h. The excess *t*-butylacrylate was distilled off under vacuum (b.p.: 30 °C/15 mm). The residue was dissolved in 200 ml of chloroform and 2 ml of dimethylformamide. 0.34 Mol (40.46 g; 24.5 ml) of thionyl chloride was added dropwise to the reaction mixture while maintaining the temperature below 40 °C. After the addition of thionyl chloride was completed, the mixture was stirred for another 0.5 h. The reaction mixture was poured into 250 ml of water containing 80 g of sodium bicarbonate. The organic layer was separated and dried over magnesium sulfate. After filtration, the solvent was removed on a Rotavapour ($T < 50$ °C).

100 g of the residue, 200 g sodium carbonate, 10 g of pentaerythritol and 200 g dibutyl phthalate were heated at 150 - 160 °C under stirring in a 500 ml three-necked flask. The reaction product was distilled off under vacuum, purified by fractional distillation and dried over calcium hydride (b.p. 46 °C/1 mm).

Overall yield: 19.5 g (10.5%). The ^1H NMR spectrum (Fig. 1) is in accordance with the structure.

Fig. 1. 360 MHz ^1H NMR spectrum of *t*-butyl-3-azetidinypropionate in CDCl_3 .

Synthesis of the polymers

Under the influence of cationic initiators, monomers (1) and (2) undergo polymerization to the corresponding poly[*N*-(2-alkoxycarbonylethyl)imino-trimethylene].

At 80 °C, polymerization in bulk with methyl triflate is almost quantitative after 24 h.

A typical procedure is as follows: to 2 g (1.08×10^{-2} mol) of (2) 24.47 μl (2.16×10^{-4} mol) of methyl triflate is added. The ampoule is degassed three times, sealed in vacuum, and stirred during 24 h in a bath thermostatted at 80 °C; 2 g of poly-(2) with a $\bar{M}_N$ of 8200, as measured by VPOM, is obtained.

Oxidative coupling

In our batch-type reactor the following standard reaction conditions were used for the oxidative coupling of DMP: $T = 298.15$ K, $[\text{Cu}^{2+}] = 3.32 \times 10^{-3}$ mol dm $^{-3}$, $[\text{DMP}] = 0.06$ mol dm $^{-3}$, $P_{\text{O}_2} = 101.3$ kPa, total reaction volume = 0.015 dm 3 , shaking speed of reaction vessel = 4 - 5 Hz, solvent mixture 1,2-dichlorobenzene:methanol = 13:2 (v/v). In order to determine the complex with optimum catalytic activity, the concentrations of added polymeric amine ligands and hydroxyl ions were varied.

The cylindrical reaction vessel was connected with an automatic gas burette supplied with pure O $_2$ [8]. After saturation of the catalyst solution with O $_2$ the reaction was started by adding the substrate DMP, and the vessel was violently shaken in a thermostatted bath. The shaking speed was high enough to prevent dioxygen diffusion from the gas phase from becoming rate-determining [15]. The dioxygen consumption was recorded at constant pressure as a function of reaction time. The initial reaction rate R_0 was calculated from the initial slope of this dioxygen consumption curve.

After dilution with solvent mixture, DPQ concentrations in the reaction mixtures were determined with a Pye Unicam SP 8-200 UV/Vis spectrophotometer at 425 nm ($\epsilon = 61\,000$ dm 3 mol $^{-1}$ cm $^{-1}$).

Adsorption experiments

A known amount of silica was added to solutions of the polymer in appropriate mixtures of 1,2-dichlorobenzene and methanol. The silica was suspended by gentle ultrasonification with a Sonifier B-12 (Branson Sonic Power Company) for 2 - 3 min at 40 W power. Under these conditions, mechanical degradation of the low molar mass polymers we were using ($\bar{M}_w = 8000 - 20\,000$ g mol $^{-1}$) appeared to be negligible. The suspensions were put into closed flasks, and the polymer was allowed to adsorb during

20 h under gentle shaking at room temperature. A period of 20 h is generally sufficient to reach equilibrium [19 - 22]. After the adsorption period, a solution of a known amount of $\text{CuCl}_2 \cdot 2 \text{H}_2\text{O}$ in a small volume of methanol was added to the suspensions. The mixtures immediately turned yellow, the colour of the catalytically active complex, and were shaken for 10 min. An aliquot was centrifuged at 5000 rpm for 20 min, and the supernatant was decanted. Since the UV adsorption maximum of the polymeric complex was not stable with time, a known volume of the supernatant was exhaustively extracted with a known volume of an aqueous Na_4EDTA solution (4 g Na_4EDTA per dm^3). The aqueous and 1,2-dichlorobenzene phases were separated by centrifugation (5000 rpm, 15 min), after which no Cu^{2+} was detectable in the organic layer. The UV absorption of the Cu^{2+} -EDTA complex was measured at 725 nm with a Pye Unicam SP 8-200 UV/Vis spectrophotometer. From the absorption, the total amount of Cu^{2+} present in the total amount of supernatant could be calculated after correction for dissolution of methanol in the aqueous phase. We were also able to calculate in this way the total amount of Cu^{2+} present at the silica. The silica with the adsorbed Cu^{2+} -polymer complexes was dried in open air at room temperature by allowing the volatile solvent mixture to evaporate. The weight contents of nitrogen and pure SiO_2 were determined by elemental analysis. From these data we could calculate the amount of polymer adsorbed on the silica.

Another portion of the samples in the closed flasks was used for catalytic experiments within 15 min after the addition of the CuCl_2 solution. The suspensions were quantitatively transferred to the reaction vessels, DMP was added and the dioxygen consumption was measured.

Re-use of the catalyst

Once the immobilized catalyst had been used in a catalytic experiment the reaction mixture was centrifuged, the supernatant containing the products was decanted and new solvent mixture was added to the catalyst. After suspending the material and saturating with dioxygen, new substrate was added and the dioxygen consumption was determined again.

Results and discussion

Reactions in the absence of silica

In order to determine the optimum conditions for the catalysis, the initial dioxygen consumption rate R_0 was measured as a function of the polymeric amine ligand: Cu^{2+} ratio, without the addition of adsorbent. Figure 2 shows an optimum activity at a N/Cu ratio of ~ 4 . However, because of steric hindrance it is unlikely that all amine ligands of the polymer chain participate in the formation of the complex. This idea was supported by building molecular models of the complex. Thus, a real N/Cu ratio of 2, as found for TMED [7], cannot be excluded. Moreover, it should

Fig. 2. Initial dioxygen consumption rate R_0 as a function of the N/Cu ratio under standard conditions. No addition of OH^- , $\bar{M}_w(1) = 8000$.

Fig. 3. Possible schematic structure of the copper complex of polymer (1) with N/Cu = 4. (.....) = ester carbonyl-copper interactions.

be noted that the Cu^{2+} ions may also interact with the ester carbonyl groups [23]. Although the exact structure of the complex is of less importance to us in this study, we may draw a possible structure, assuming that the copper ions mainly interact with the nitrogen atoms of the polymer chain, and assuming that a binuclear complex is formed, as with TMED [7] (see Fig. 3).

The catalytic activities of most investigated polymeric Cu^{2+} catalysts for the oxidative coupling of phenols increased on addition of hydroxyl ions. In fact there was often no catalytic activity at all in the absence of OH^- , and added hydroxyl ions were mostly used to form a more active complex [7 - 10, 14 - 16, 24, 25]. In order to find out whether hydroxyl ions also exhibit an accelerating effect on our present complex, the initial dioxygen consumption rate R_0 was determined as a function of the OH^-/Cu ratio. The results are presented in Fig. 4 for the optimum N/Cu ratio of 4 derived from Fig. 2. The hydroxyl ions were added as solutions of KOH in methanol, and the yellow colour of the fresh complex solutions immediately turned green. From Fig. 4 we see that our complexes are most active without the addition of hydroxyl ions. It is also clear that the addition of greater amounts of hydroxyl ions has a disastrous effect on the catalytic activity of our complex. A possible explanation for this loss of catalytic activity may be the hydrolysis of the ester groups of our polymer chains, which leads to less active complexes. If we look more carefully at Fig. 4, we can see that for $\text{OH}^-/\text{Cu} \leq 0.3$ the catalytic activity remains practically constant. However, it is unlikely that in this region hydrolysis does not occur. Thus it is still possible that the addition of hydroxyl ions would also accelerate the oxidative coupling of DMP by our complex, but because of the hydrolysis of ester groups such acceleration is not observed.

The selectivity of our catalyst for PPO formation was determined under standard conditions with N/Cu = 4.0 and $\text{OH}^-/\text{Cu} = 0$. After the reaction was complete, the DPQ concentration was determined by UV spectroscopy. It

Fig. 4. Initial dioxygen consumption rate R_0 as a function of the OH/Cu ratio. Standard conditions with $N/Cu = 4$, $\bar{M}_{W, (1)} = 8000$.

Fig. 5. Initial dioxygen consumption rate R_0 as a function of dioxygen pressure. Standard conditions with $N/Cu = 4$ and no addition of OH^- , $\bar{M}_{W, (1)} = 8000$.

appeared that 60% PPO and 40% DPQ were produced. Thus, the selectivity is rather low. Meinders and Challa were able to improve the selectivity of binuclear copper/TMED complexes by OH^- addition [9], but we couldn't do so because of the mentioned hydrolyzability. For instance, Meinders and Challa found about 30% PPO yield for $N/Cu = 2$ and $OH/Cu = 0.1$ (for $OH/Cu = 0$ there was no activity) and about 80% PPO for $N/Cu = 2$ and $OH/Cu = 1.0$. Our polymer (1)-based catalyst could also yield about 80% PPO in the absence of hydroxyl ions if a higher N/Cu value of 10 was chosen.

It is known that under certain conditions and for some types of catalysts the reoxidation of Cu(I) to Cu(II) becomes rate-determining in the oxidative coupling cycle in Scheme 2 [24, 25]. To verify that we are dealing with real phenol oxidation rates under standard conditions, R_0 was measured as a function of dioxygen pressure.

Figure 5 demonstrates that variations in dioxygen pressure from 85 to 154 kPa did not alter the reaction rate. Thus for DMP concentrations up to 0.06 mol dm^{-3} we are actually measuring phenol oxidation rates.

Adsorption experiments

From the kinetic experiments described above it became clear that the copper complex of polymer (1) is an interesting catalyst for the oxidative coupling of DMP that works well without the addition of hydroxyl ions. Because of the presence of polar groups in the polymer chain, we thought that it might be possible to have the chains adsorbed on hydrophilic silica by an interaction with the SiOH groups. In this way the catalyst could perhaps be immobilized and separation of reaction products and catalyst as well as re-use of the catalyst might be possible.

The fraction of polymer that adsorbs on silica was determined for two different molecular masses of polymer (1), different amounts of silica and different solvent compositions. The results are listed in Table 1. The data in this Table indicate how to best immobilize our polymer catalyst. First, it

TABLE 1

Fraction of total added amount of polymer (1) (31.3 mg) adsorbed on the silica and total adsorbed amount on 1 g of silica (*A*)

Silica (mg)	Polymer ^a adsorbed (%)	<i>A</i> (mg g ⁻¹)	Silica (mg)	Polymer ^b adsorbed (%)	<i>A</i> (mg g ⁻¹)	Silica (mg)	Polymer ^c adsorbed (%)	<i>A</i> (mg g ⁻¹)
180.8	100	173	181.8	93	160	182.8	38	65
96.0	67	218	45.4	35	241	91.6	18	62
53.2	49	288	14.4	26	565	67.2	14	65
23.6	26	345	9.0	16	556	20.6	5	76
12.0	19	496	4.5	11	765	5.7	2	110
6.4	14	685						

Conditions: room temperature, N/Cu = 4, no OH⁻ and DMP, [Cu²⁺] = 3.32×10^{-3} mol dm⁻³ (added after the adsorption period), 0.015 dm³ of solvent.

^a $\bar{M}_w$ = 8000, 13.3 vol.% methanol in 1,2-dichlorobenzene.

^b $\bar{M}_w$ = 20 000, 13.3 vol.% methanol in 1,2-dichlorobenzene.

^c $\bar{M}_w$ = 20 000, pure methanol.

can be seen that adsorption is fairly independent of molecular weight, at least in our region of $\bar{M}_w$. Furthermore, the methanol content of the solvent mixture should be as low as possible, for from the good solvent methanol the adsorption is very incomplete. Another disadvantage of too much methanol is the fact that precipitation of the reaction product PPO may occur, which would disturb experiments with immobilized catalysts. Some methanol, however, is absolutely necessary because of the insolubility of the copper salt in pure 1,2-dichlorobenzene. Table 1 shows that from a solvent mixture with 13.3 vol.% of methanol, (almost) complete adsorption is possible if at least 180 mg of hydrophilic silica is used. The total surface of this amount of non-porous silica (containing $1.3 - 2.4 \times 10^{20}$ SiOH groups) is just sufficient to have the standard amount of 31.3 mg of polymer (consisting of 1.2×10^{20} monomeric units) adsorbed in a flat monolayer.

It is very likely that the polymer is adsorbed through hydrogen bonding of the amine nitrogen atoms and the ester carbonyl groups with the silanol groups of the silica surface [19 - 22, 26 - 28]. From adsorption theory it is known that the conformation of an adsorbed polymer chain exists of trains, loops and tails [29, 30]. After reaching adsorption equilibrium the fraction of segments present in trains attains a constant mean value. We must realize, however, that we are always dealing with a time-averaged conformation, and that train segments may exchange with loop and tail segments. This is also true in the presence of copper ions.

From the data in Table 1 it was clear that in 13.3 vol.% of MeOH, 180 mg of hydrophilic silica are needed for further immobilization experiments. First, the complexation of the adsorbed polymer with Cu²⁺ ions was investigated. Therefore, after the adsorption period, Cu²⁺ ions were added to the suspension, and after 10 min the fraction of Cu²⁺ ions present in the supernatant was determined. For $\bar{M}_{w,(1)} = 8000$, 99% of the added copper

ions had formed complexes with the amine ligands immobilized by the adsorbent on which 100% of the polymer was present. Thus, in the layer of adsorbed polymer an overall ratio of $N/Cu \cong 4$ was maintained. For $\bar{M}_{W,(1)} = 20\,000$, 93% of the copper ions had disappeared from the supernatant while also 93% of the polymer was present on the silica. So the overall N/Cu ratio was again approximately 4. An adsorption experiment with 180 mg of silica in a solution of $CuCl_2 \cdot 2 H_2O$ in 13.3 vol.% of methanol showed that copper ions do not adsorb on the silica by themselves, but rather they are forced towards the silica by the immobilized amine ligands.

In Fig. 6 the adsorbed amount of polymer (1) per gram of silica (A) is plotted as a function of the added amount of silica. The total amount of polymer was kept constant (31.3 mg, the standard amount for $N/Cu = 4$). Of course, A should gradually increase with increasing amounts of homodisperse polymer per gram of silica [29]. However, Fig. 6 shows that independent of the $\bar{M}_W$ an extraordinary increase of A occurs with increasing amounts of polymer per gram of silica in the methanol/1,2-dichlorobenzene solution. In order to explain this, the degree of polydispersity $D (= \bar{M}_W/\bar{M}_N)$ should be taken into account. For the material with $\bar{M}_W = 8000$, D equals about 2.0, and for $\bar{M}_W = 20\,000$ D equals about 2.5. When enough silica is present to adsorb the total amount of polymer, then almost all molecules will adsorb irrespective of their molar mass. However, when the total adsorbent surface is insufficient, fractionation can take place [27, 31]: as long as longer molecules are present in solution than present on the silica

Fig. 6. Total adsorbed amount of polymer (1) on 1 g of silica (A) as a function of the amount of hydrophilic silica used. In all experiments 31.3 mg of polymer was used. (●): $\bar{M}_W = 8000$ in 13.3 vol.% methanol in 1,2-dichlorobenzene; (○): $\bar{M}_W = 20\,000$ in 13.3 vol.% methanol in 1,2-dichlorobenzene; (■): $\bar{M}_W = 20\,000$ in pure methanol.

surface, the lower molar mass material is displaced from the surface by the higher molar mass material. Longer molecules adsorb with longer loops and tails [30]; thus, the very strong increase in A with decreasing amounts of silica is due to an increase in average molar mass of the adsorbance. Finally, in a good solvent the dependence of the adsorbance (A) on the molar mass (or MWD) should be very small [31], which is in fact demonstrated in Fig. 6 for the good solvent methanol.

To be certain that our adsorbed catalyst cannot be displaced from the silica surface by the PPO produced during the oxidative coupling reaction (maximum amount about 80 mg), we investigated the adsorption of PPO on Aerosil 380 V from the standard reaction solvent mixture. These adsorption experiments were carried out as described earlier (see Experimental). The amount of PPO present on the centrifuged silica was determined by elemental analysis. When an excess of PPO (about 100 mg) and 180 mg of silica was used, only 17% of the PPO was adsorbed. As the standard amount of our polymeric catalyst (31.3 mg) adsorbs completely on the same amount of silica under the same conditions (see Table 1), the mentioned displacement of catalyst from the silica surface is very unlikely.

Kinetic measurements; comparison of unbound and immobilized catalyst

We consider only experiments in which adsorption of the polymer ligand is complete, or nearly complete, and in which the overall N/Cu ratio on the adsorbent is 4. In these situations, the overall N/Cu ratios are like those earlier in the absence of silica, and an eventual difference in activity as compared with unbound catalysts cannot be due to a differing overall N/Cu ratio.

In order to demonstrate that the adsorption of the polymeric copper complex and the adsorption of the naked polymer chain after subsequent addition of copper are alike, both were allowed to adsorb on 180 mg of silica in 13.3 vol.% of methanol in 1,2-dichlorobenzene for a period of 15 min. Immediately after this period, copper ions were added to the adsorbed naked polymer chains to form the complex, and the dioxygen consumption rates were determined. Within experimental error, there was no difference between the measured activities.

Since we are measuring real oxidation rates of DMP with the step of k_2 (Scheme 2) as rate-determining, Lineweaver-Burk plots of R_0^{-1} versus $[S_0]^{-1}$ could be constructed by performing substrate concentration-dependent measurements. The plots are shown in Fig. 7. From these plots we can estimate the reaction rates at infinite substrate concentration (*i.e.* the reciprocal intercept). Moreover, for unbound catalyst we may assume that all copper ions participate in the formation of active complexes and we are able to calculate k_2 and K_m^{-1} . The values of $R_{\max}$, k_2 and K_m^{-1} are listed in Table 2.

For unbound catalyst the measured reaction rates are almost independent of $\bar{M}_w$, and one Lineweaver-Burk plot was constructed from which $R_{\max}$, k_2 and K_m^{-1} were calculated. The k_2 value found of 0.026 s^{-1} is higher

Fig. 7. Lineweaver-Burk plots for the copper complexes with polymer (1). Standard conditions with $N/Cu = 4$. (■): unbound catalyst with $\bar{M}_W = 8000$; (□): unbound catalyst with $\bar{M}_W = 20\,000$; (●): catalyst with $\bar{M}_W = 8000$ after adsorption on 180 mg of hydrophilic silica; (○): catalyst with $\bar{M}_W = 20\,000$ after adsorption on 182 mg of hydrophilic silica.

TABLE 2

$R_{\max}$ and values of k_2 and K_m^{-1} as calculated with eqn. (1) from the Lineweaver-Burk plots of Fig. 7. Standard conditions with $N/Cu = 4$

Catalyst system	$\bar{M}_W$	$10^6 R_{\max}$ ($\text{mol dm}^{-3} \text{s}^{-1}$)	k_2 (s^{-1})	K_m^{-1} ($\text{dm}^3 \text{mol}^{-1}$)
unbound polymer (1)	8000 and 20 000	± 87	0.026	35.5
polymer (1) on 180 mg of silica	8000	40.5	—	—
polymer (1) on 182 mg of silica	20 000	46.3	—	—

than the value found for copper complexes of poly(styrene-co-4-vinylpyridine) ($k_2 = 0.015 \text{ s}^{-1}$) [32], but significantly lower than the value found for copper complexes of poly(styrene-co-*N*-vinylimidazole) ($k_2 = 0.13 \text{ s}^{-1}$) [24]. Table 2 shows that the immobilization procedure reduces $R_{\max}$ by $\sim 50\%$. To attempt to explain the observed activity loss, we must consider that part of the train segments may interact with the surface silanol groups through the ester carbonyl groups. In principle, the nitrogen atoms of such train segments may be still available for coordination with Cu^{2+} . As the adsorbed train segments are very stiff, the configurational transition in the rate-determining step from planar Cu(II) to tetrahedral Cu(I) during the electron transfer process between substrate and copper [32] might be hindered. Therefore, these complexes are less active than those present in the flexible loops and tails. In addition, the train segments may interact with the silanol groups through their nitrogen atoms [28]. These nitrogens lose their free electron

pairs and can no longer participate in complex formation. Consequently, the effective local N/Cu ratio along the adsorbed polymer chains will be lower than the overall value of 4. In view of Fig. 2, this will lead to a lower activity.

The observation that the value of $R_{\max}$ of the adsorbed catalyst is more or less independent of its molar mass (see Table 2 and Fig. 7) is in complete agreement with the sophisticated adsorption theory of Scheutjens and Fleer [29, 30]. This theory predicts that at a given adsorbed amount of catalyst, there is no molar mass dependence of the structure in the adsorbed layer. Therefore the amount of segments in trains, sometimes referred to as 'direct surface coverage', will be practically the same for the high and low molar mass catalysts. Thus, by simply determining the adsorbed amount of catalyst and measuring catalytic activities, one should be able to obtain information on the conformation of the immobilized polymer catalyst.

Finally, the slightly higher activity of the polymer catalyst with $\bar{M}_w = 20\,000$ as compared with the catalyst with $\bar{M}_w = 8000$ may be explained as follows. From Fig. 3 it is obvious that chains with *e.g.* less than 8 segments will not be able to form the optimum intramolecular binuclear copper complexes. For the sample with $\bar{M}_w = 8000$ the fraction of such short chains is larger, and hence the total activity will be lower.

Re-use of the catalyst

After carrying out recycling experiments with the catalyst based on polymer (1) with $\bar{M}_w = 8000$, it appeared that the catalyst was still active, although 40 - 50% of the activity had been lost. Thus, in principle, separation of products and catalyst as well as re-use of the catalyst is made possible by our immobilization procedure.

The drop in activity after re-use can be ascribed predominantly to hydrolysis of the ester groups of our polymeric ligand, which was more pronounced in the case of added hydroxyl ions (Fig. 4). A slight extra O_2 consumption pointed to the possibility that oxidation of the polymeric copper complex (at the $\alpha\text{-CH}_2$ position with respect to the nitrogen atom) may also result in some loss of activity. However, a fresh solution of the catalyst based on polymer (2) (see below) did not consume any dioxygen during a shaking period of 3 h under standard conditions, and after subsequent DMP addition the normal dioxygen consumption rate was observed, *viz.* $\sim 33 \times 10^{-6} \text{ mol } O_2 \text{ dm}^{-3} \text{ s}^{-1}$.

The hydrolysis may be accelerated near the silica surfaces due to water enrichment around the silica spheres as described by Verlaan *et al.* [16]. Experiments showed that on standing for several hours the activity of the complex is strongly reduced (see Fig. 8), while the yellow colour of the fresh complex slowly turns green. The same green colour appears immediately on addition of hydroxyl ions to a fresh complex solution. On standing for several days, the polymer even becomes soluble in water.

In order to improve the recyclability of our polymeric copper complexes, analogous polymeric ligands carrying *t*-butyl ester groups instead of ethyl ester groups were synthesized. The former are much more stable

Fig. 8. Initial dioxygen consumption rate R_0 as a function of previous hydrolysis time of the polymeric copper complexes. Standard conditions with $N/Cu = 4$. (●): poly[*N*-(2-ethoxycarbonylethyl)iminotrimethylene] with $\bar{M}_W = 8000$; (○): poly[*N*-(2-*t*-butoxycarbonylethyl)iminotrimethylene] with $\bar{M}_N = 8200$.

towards hydrolysis [33], and from Fig. 8 it can be concluded that the *t*-butyl based catalyst should be more suitable for recycling experiments, provided that these are carried out within 8 h (for longer times its activity becomes considerably lower and the same green colour observed with polymer (1) appears). The re-use experiments were carried out under standard conditions with $N/Cu = 4$ and without addition of OH^- . The results were disappointing, as the catalyst lost about 75% of its activity on re-use although enough hydrophilic silica was added to allow complete adsorption and adsorption equilibrium must have been achieved. In view of Fig. 8 we can ascribe this tremendous loss of activity mainly to incomplete adsorption of the poly[*N*-(2-*t*-butoxycarbonylethyl)iminotrimethylene] chains, which is probably due to a shielding of the ester carbonyl groups. An adsorption experiment showed that 51% of the polymer was adsorbed. Even when the amount of polymer was halved, only 63% of it was immobilized by the same amount of silica. This weaker adsorption is in agreement with the observed smaller decrease in activity on addition of silica as compared with the ethyl-based catalyst having $\bar{M}_{W(1)} = 8000$, viz. ~40 and 65% respectively under standard conditions.

The lower initial activity of the fresh *t*-butyl-based catalyst might be ascribed to the bulkiness of the *t*-butyl groups, considering that some interference of the ester side groups with the active copper centers exists (Fig. 3).

Conclusions

The copper complex of poly[*N*-(2-ethoxycarbonylethyl)iminotrimethylene] is a moderately active catalyst for the oxidative coupling of 2,6-dimethylphenol and can be well immobilized by simple adsorption on hydrophilic silica. The loss in catalytic activity caused by this immobilization procedure is practically independent of the molar mass of the polymer catalyst.

At standard conditions (see experimental) our system follows the Michaelis–Menten type of reaction kinetics for both unbound and immobilized catalysts. For unbound catalyst the rate-determining rate constant is $k_2 = 0.026 \text{ s}^{-1}$. For adsorbed catalyst the number of active catalytic sites is not known precisely, so no reliable k_2 value can be obtained.

The catalyst is active without the initial addition of hydroxyl ions, which is very unusual. The selectivity of our catalyst for PPO formation is rather low: 60 - 80% of the reaction products. This is caused by the fact that no OH^- can be applied.

The disadvantage of our system is the hydrolizability of the catalyst. Although we are able to separate our immobilized catalyst from the reaction products, which was our main aim, re-use of the catalyst is only possible with a significant loss of activity. The hydrolysis can considerably be suppressed by substituting t-butyl ester groups for the ethyl ester groups on the catalyst. The disadvantage of this transformation, however, is a decreasing adsorption power, and therefore re-use of the catalyst is only possible with a loss of activity which was even greater than for the ethyl-based catalyst. Thus it seems necessary to seek a better method for binding the t-butyl-based polymeric catalyst to the silica in order to make use of its greater chemical stability.

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