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A spectacular increase in the polymerisation rate of 2,6-dimethylphenol induced by acetonitrile

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Abstract

The oxidative polymerisations of 2,6-dimethylphenol with copper-(1-methylimidazole) complexes as the catalyst precursor compounds in different solvents showed the catalysts to be extremely active when using acetonitrile. Acetonitrile can act as a labile ligand for copper and also prevent the catalyst to become poisoned due to hydrolysis. Addition of increasing amounts of water leads to a progressive deactivation of the catalyst. © 2001 Published by Elsevier Science Ltd.

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1. Introduction

A wide variety of metalloenzymes are found in nature which act as catalysts to perform biotransformations [1]. Enzymatic syntheses often proceed under mild conditions and are very selective. It is therefore interesting to study and model these bio-catalysts in order to use them as effective chemical tools for common organic reactions.

The copper-catalysed polymerisation of 2,6-dimethylphenol **1** (DMP) leading to poly(1,4-phenylene ether) **2** (PPE), an industrial amorphous high-performance thermoplastic, and undesirable 4-(3,5-dimethyl-4-oxo-2,5-cyclohexadienylidene)-2,6-dimethyl-2,5-cyclohexadienone **3** (DPQ) (Fig. 1) is known for more than 40 years [2].

PPE has excellent mechanical properties. It is chemically resistant even at elevated temperatures and it is moisture resistant [3,4]. PPE is a very important and valuable engineering plastic [5] used in computer housings, television housings, keyboard frames, interface boxes and so on. This polymerisation reaction has been extensively studied [6] and early proposals involve mononuclear copper–phenoxo complexes as active species [7,8], whereas recent ones advocate dinuclear copper–phenoxo complexes producing phenoxonium cations as active species [9–16]. The reaction mechanism is obviously not yet fully clarified. It is therefore necessary to study further this mechanism, also with the aim to optimise the catalytic activity.

This paper reports important improvements which have been achieved by modifying several reaction parameters, like solvent polarity and solvent hydrophilicity.

2. Experimental

2.1. Materials

All reagents were commercially available compounds and were used as received except that DMP was recrystallised from *n*-hexane.

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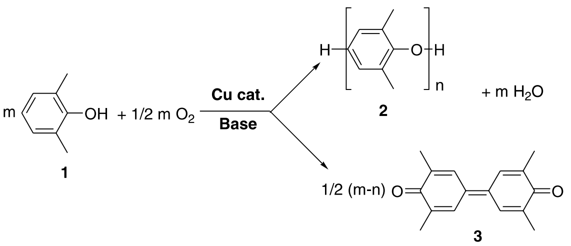

Fig. 1. Copper-catalysed oxidative coupling of DMP.

2.2. *Molecular weights of poly(2,6-dimethyl-1,4-phenylene ether)*

The size exclusion chromatography (SEC) measurements were carried out with multiple detection consisting of an interferometric RI detector (Optilab DSP, Wyatt Technology) in series with a multi angle light scattering detector (Dawn-DSP-F, Wyatt Technology). With this configuration absolute molecular weights are obtained on-line. The PPE samples were measured on two Mixed-C columns (Polymer Laboratories) in chloroform with a flow of 1 ml min^{-1}. The concentration was 10 mgml^{-1}; sample load was 100 μl.

2.3. *Dioxygen-uptake measurements*

A typical catalyst solution was prepared by dissolving, in a 10 ml volumetric flask, 24.2 mg (0.1 mmol) of $Cu(NO_3)_2 \cdot 3H_2O$ in 5 ml of acetonitrile, adding 0.24 ml (3.0 mmol) of *N*-methylimidazole (Meim), and filling up to 10 ml with acetonitrile. This resulted in a 0.01 M $[Cu(Meim)_x](NO_3)_2$ solution in acetonitrile. The substrate solution was prepared *just before* use by dissolving, in a second 10 ml volumetric flask, 366.5 mg (3.0 mmol) of DMP (**1**) in 5 ml of acetonitrile, adding 20 μl (0.1 mmol) of sodium methoxide (30% solution in methanol), and filling up to 10 ml with acetonitrile, which resulted in a 0.3 M solution of DMP and a 0.01 M solution of NaOMe in acetonitrile. In a typical quantitative, time-resolved dioxygen-uptake experiment, one compartment of a special two-compartment reaction vessel was filled with 5 ml of the 0.01 M copper(II)/Meim solution, and the other with 10 ml of the substrate solution. The resulting reaction mixture was 3.33 mM in copper and 0.2 M in DMP (**1**). All polymerisation reactions were performed at 25°C under pure dioxygen at atmospheric pressure. These are the conditions referred to as standard conditions, which furthermore imply a Meim/Cu ratio of at least 30 and a NaOMe/Cu ratio of 2. The reaction selectivity could be determined by diluting 1 ml of the reaction mixture with toluene and measuring the UV absorbance of DPQ (**3**) at 421 nm. A detailed description of the dioxygen-uptake experiments and the processing of the experimental data have been previously published [13,17,19].

3. Results and discussion

3.1. *Solvent effect on the polymerisation rates*

Previous investigations [14,19] have clearly shown the effectiveness of (Meim)copper(II) complexes as catalysts in the oxidative coupling of DMP (**1**) in toluene/methanol (13/2 v/v). New results obtained, using a selection of common solvents, are reported in Table 1.

No significant catalytic activity improvement was observed in DMF, propionitrile, phenylacetonitrile or THF. However, a spectacular improvement was obtained in acetonitrile, as the initial dioxygen absorption rate R_0 increased from 45 to 197×10^{-5} $mol l^{-1} s^{-1}$. This spectacular effect of acetonitrile on the activity is quite surprising and has hitherto not been reported. Although acetonitrile is a rather labile ligand, its weak donor properties might nevertheless be responsible for the substantial increase in reaction rate. In that case one would expect other nitriles to have an analogous influence. However, the use of propionitrile led only to a R_0

Table 1
Observed initial polymerisation rates in different solvents using [Cu(*N*-methylimidazole)$_4$](NO$_3$)$_2$ and *N*-methylimidazole as catalyst precursor

Solvent	% Conversion[a]	Reaction time (h)	R_0 (10^{-5} $mol l^{-1} s^{-1}$)	$10^4 f_{O_2}$[b]
Phenylacetonitrile	7	2.07	–	–
Propionitrile	97	0.53	12	–
Tetrahydrofuran	99	0.65	18	–
Dimethylformamide	69	2.23	26	3.65
Toluene/MeOH (13/2 v/v)	100	0.50	45	9.08[c]
Acetonitrile	100	0.10	197	4.32

[a] The conversion of DMP (**1**) was based on the amount of dioxygen absorbed in this time. Selectivity in PPE (**2**) was always found to be over 95%.

[b] Solubility of dioxygen calculated from the ΔG^0 values for solution of O_2 in each solvent [18].

[c] f_{O_2} value for toluene. The value is 4.18 for methanol.

value of 12×10^{-5} $\mathrm{mol\,l^{-1}\,s^{-1}}$ and the use of phenylacetonitrile to almost no activity at all.

Acetonitrile is quite hydrophilic and could therefore avoid the poisoning of the catalyst from the water produced during the reaction, by scattering it from the copper coordination sphere. A similar influence on the catalytic activity should have been exerted with THF, but this was not the case, as only an R_0 of 18×10^{-5} $\mathrm{mol\,l^{-1}\,s^{-1}}$ was reached. This lower value for THF is probably due to the extremely low ligand donor properties of THF, which prevents it to act as a ligand to copper in the reaction circumstances. Finally, this five-fold increase in reaction rate could be due to a much greater availability of dioxygen, as a consequence of a possible greater solubility of dioxygen in acetonitrile. However, solubility values found in the literature [18] showed that dioxygen is even better soluble in toluene than in acetonitrile (Table 1).

3.2. Acetonitrile effect on the reaction

To further study the "acetonitrile effect", polymerisations of DMP (**1**) were also performed in solvent mixtures. Different amounts of acetonitrile were mixed in toluene, because toluene is an industrially more suitable solvent. Furthermore, because PPE is soluble in toluene and not in acetonitrile, the possible confinement of the copper catalyst in precipitated PPE and thereby a drop of the catalytic activity, will be avoided. The results are listed in Table 2.

These results show clearly the huge increase in catalytic activity with a significant slope increment with increasing percentage of acetonitrile.

However, PPE starts to precipitate after the addition of only 30% acetonitrile to toluene. So, from an industrial point of view, a minimum of 20% acetonitrile is necessary to have a homogeneous reaction mixture, but then the catalytic activity will probably not be high enough.

3.3. The effect of water on the catalytic activity

Water is a co-product of the oxidative coupling of DMP (Fig. 1). In our reaction conditions, 0.36% of water in acetonitrile is produced after completion of the polymerisation. From previous work [19] it is known that some water is needed for the reaction to start, but also that too much water will lead to a copper-catalyst poisoning through the formation of inactive copper(II) hydroxide. Thus, different amounts of water were added to acetonitrile to establish the minimum of water amount required to "kill" the catalyst. Fig. 2 shows the results obtained. Surprisingly still an R_0 of 20×10^{-5} $\mathrm{mol\,l^{-1}\,s^{-1}}$ was observed with as much as 47% of water in acetonitrile. This value was already reached with 13% of water, which might correspond to water saturation of the copper complex. Nevertheless, water is a poison as only an addition of 3% water showed a 75% loss in activity from 197 to 5×510^{-5} $\mathrm{mol\,l^{-1}\,s^{-1}}$, although a complete stop appears not to be possible with water.

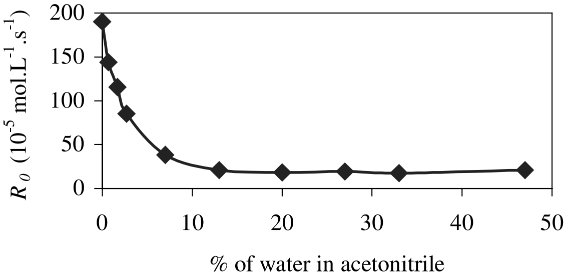

Fig. 2. Effect of added water on the initial dioxygen uptake in acetonitrile.

4. Conclusions

The ligand *N*-methylimidazole combined with acetonitrile as the solvent is a very efficient catalytic system. Acetonitrile induces a spectacular increase of the initial dioxygen-uptake rate R_0 (from 35 in toluene/acetonitrile (9/1 v/v) to 197×10^{-5} $\mathrm{mol\,l^{-1}\,s^{-1}}$ in pure acetonitrile). It seems that acetonitrile plays an important role as a labile ligand and by favouring water scattering and so avoiding catalyst poisoning. Increasing the water amount by more than 3% in acetonitrile leads to a 75% drop of catalytic activity (up to a value around 20×10^{-5} $\mathrm{mol\,l^{-1}\,s^{-1}}$).

Table 2
Effect of acetonitrile amount (%) in toluene on catalytic activity

%CH_3CN in toluene	10[a]	20[a]	30[b]	40	50	60	70	80	90	100
Reaction time (h)	1.52	1.13	0.43	0.22	0.15	0.17	0.10	0.10	0.10	0.10
%Conversion[c]	99	99	98	100	99	100	99	99	100	100
R_0 (10^{-5} $\mathrm{mol\,l^{-1}\,s^{-1}}$)	35	44	59	76	112	118	129	142	169	197

[a] For these cases, PPE formed were completely soluble in the solvent mixture.

[b] PPE formed was partially soluble.

[c] All polymers obtained had a M_w from 20,000 to 40,000 D (measured with SEC).

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