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The Oxidative Coupling of 2,6-Xylenol Catalyzed by Polymeric Complexes of Copper, 2^{*})

Physicochemical Study on Copper(II) Complexes of Partially Dimethylamino-methylated Polystyrene

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SUMMARY:

The polymeric catalyst formed by complexation of copper(II) chloride and partially dimethylaminomethylated polystyrene was investigated to explain its behaviour in the oxidative coupling of 2,6-xylenol (3). Viscometric studies indicated that at low polymer concentrations coordination of tertiary amine groups to copper(II) causes an intramolecular crosslinking. UV measurements and preliminary results of ESR point to a dimeric structure of these complexes with two amine groups per copper. A mechanism for the action of this polymeric catalyst is suggested, based on these results and on those described in Part 1. It appeared that some "free" copper(II) is essential for the catalytic activity, without which the reoxidation of copper(I) cannot take place.

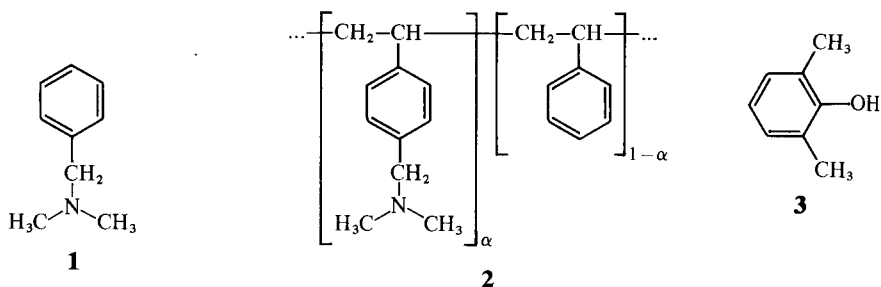
Introduction

Oxidative coupling of 2,6-xylenol (3) catalyzed by copper/amine catalysts has been the subject of many investigations^{1,2)}. Mostly the reactions are carried out at high amine to copper ratios, sometimes even the amine being the solvent. Under these conditions poly(oxy-2,6-dimethyl-1,4-phenylene) is the main reaction product and only a few percents of 2,6,2',6'-tetramethyl-1,1'-dioxo-4,4'-bicyclohexa-2,5-dienylidene (tetramethyldiphenquinone) are formed³⁾. On the other hand, if one uses low amine to copper ratios often no polymer is formed and the C—C coupling product dominates.

Up to now there seems to be no reasonable explanation for these facts. One important factor which influences the direction of the reaction is the

^{*}) Part 1: cf.⁴⁾.

steric hindrance of the ortho substituents of the phenol and the coordinated amine. Increasing the bulkiness of these substituents results in favouring C—C coupling³). In studying the oxidative coupling of **3** catalyzed by copper complexes of partially dimethylaminomethylated polystyrene (**2**), we noticed some remarkable differences in reaction rates of these complexes compared to the low molecular analogue *N,N*-dimethylbenzylamine (**1**) as it has been described in Part 1 of this series⁴).



To explain these differences we carried out further investigations and propose a possible mechanism for catalysis of the oxidative coupling of **3** by the polymeric complexes in this publication.

Experimental Part

Chemical modifications of the polystyrenes which were used have been described in Part 1⁴). Analytically pure $\text{CuCl}_2 \cdot 2\text{H}_2\text{O}$, 1,2-dichlorobenzene, and methanol were purchased from Merck; *N,N*-dimethylbenzylamine from Schuchardt.

Data of the partially dimethylaminomethylated polystyrenes

Name	\bar{M}_v	Nitrogen content in %	α (s. formula 2)
at-PSI	200000	1,21	0,10
at-PSII	20000	2,21	0,18

Viscometry

For viscometry only at-PSI was used. Viscosities were measured in an Ubbelohde viscometer with a Lauda Viscotimer at 30°C in 1,2-dichlorobenzene/methanol (6,5:1 v/v) mixtures. For the titration experiments we used a conc. HCl solution in water,

diluted with methanol. The reduced viscosities of polymer complexes at a fixed N/Cu mole ratio as function of the polymer concentration were measured with solutions obtained by dilution of the most concentrated solution.

UV measurements

The kinetic experiments were carried out in closed cells. The formation of diphenoquinone (2,6,2',6'-tetramethyl-1,1'-dioxo-4,4'-bicyclohexa-2,5-dienylidene) ($\lambda_{\text{max}} = 420 \text{ nm}$, $\epsilon = 61\,000 \text{ dm}^3 \text{ mol}^{-1} \text{ cm}^{-1}$) was followed by an "Optica CF 4R" double beam spectrophotometer. Spectra of the complexes were recorded on a "Cary 14" recording spectrophotometer between 700 and 1000 nm using an IR lamp and IR detection. All UV experiments were performed in 1,2-dichlorobenzene/methanol (6,5:1 v/v) at room temp. Kinetic experiments were carried out with at-PSI, and at-PSII was used for the spectra of the complexes.

Results

Viscometric investigations

The effect of the crosslinkages, formed by coordination of amine groups with copper(II) chloride, on the reduced viscosity of at-PSI (properties s. Exptl. Part) is shown in Figs. 1 and 2.

First of all at-PSI without copper(II) chloride (upper curve, Fig. 1) behaves quite normally; the reduced viscosity shows a straight line as a function of the concentration. Addition of copper(II) chloride to these polymer solutions has three effects. (i) At each polymer concentration the reduced viscosity becomes lower, which suggests an intramolecular crosslinking; (ii) the relation between reduced viscosity and polymer concentration is no longer linear; (iii) there is a minimum in the reduced viscosity for all polymer concentrations at mole ratio N/Cu = 1,5. The nonlinear relationship between reduced viscosity and polymer concentration could not be ascribed to a polyelectrolyte effect because addition of CsCl did not change the reduced viscosity⁵. Probably the explanation is as follows.

Dilution of a solution enhances dissociation. In our case this means dissociation of the coordination complex and subsequently a rise in viscosity because of less intramolecular crosslinking. On the other hand by concentrating the solution we approach the homogeneous segment concentration, so that crosslinking can also take place between different chain molecules (intermolecularly) which increases the viscosity. The minimum in viscosity at mole ratio

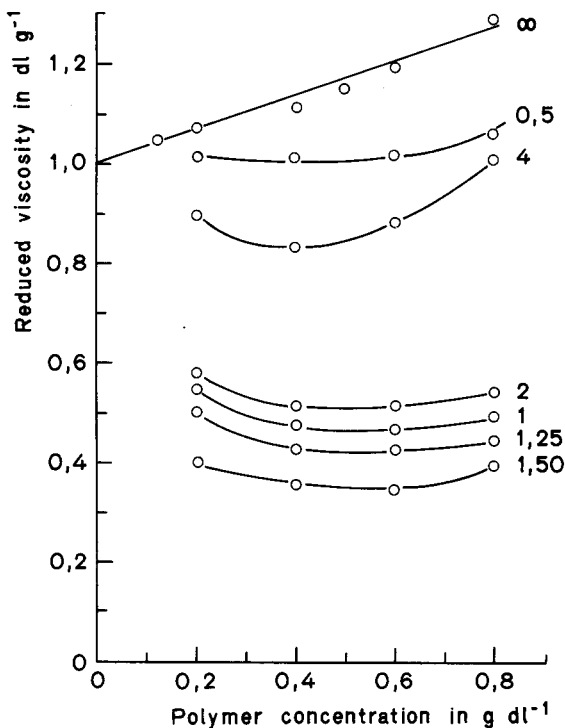


Fig. 1. Reduced viscosity as a function of [2] for different N/Cu mole ratios. The number beside the curves indicate the N/Cu mole ratios. Temperature: 30°C

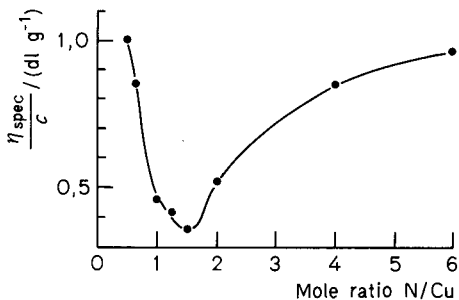
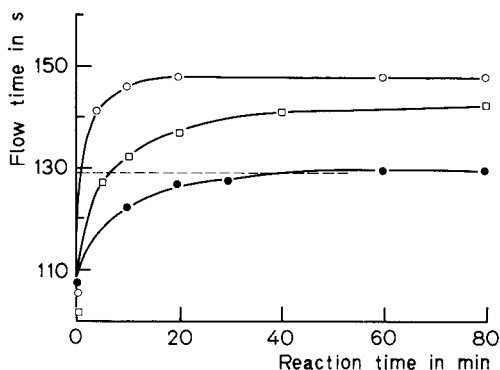


Fig. 2. Reduced viscosity as a function of N/Cu mole ratio at [2]=0.4 g dl⁻¹. Temperature: 30°C

N/Cu=1,5 points to some specific complex composition as will be discussed later. Adding 3 to solutions of different N/Cu mole ratios results in a fast increase of viscosity as can be seen in Fig. 3. The polymer concentration was constant in these experiments and therefore at higher N/Cu mole ratios less copper and less 3 was present and the rise of viscosity was correspondingly

Fig. 3. Flow time of reaction mixtures through the Ubbelohde capillary viscometer during the reaction. Mole ratio 3/Cu=16; [2]=0,4 g dl⁻¹. Mole ratios N/Cu: (○)=1, (□)=1,5, (●)=2. The dotted line corresponds to the flow time of 2 alone without copper(II) chloride or phenol. Reaction temperature: 25°C



slower. In contradiction to the results described in Part 1 the polymer complex with mole ratio N/Cu=2 does react. Moreover, the viscosity of some complexes rises above the viscosity of the neutral uncomplexed polymer. Probably the complex dissociates and the polymer becomes charged during the reaction. Titration of a polymer solution and polymer complex solutions with HCl also results in increasing viscosities as can be seen in Fig. 4. The maxima of the curves correspond to an HCl/N mole ratio of 1. Above this ratio the viscosities decrease again, because the polymers behave now as polyelectrolytes, the coils of which shrink on addition of extra electrolyte.

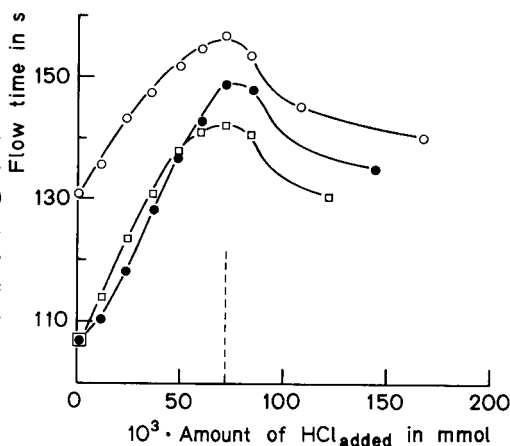


Fig. 4. Flow time through the Ubbelohde capillary viscometer of solutions of 2 with and without copper(II) chloride as function of the amount HCl added. [2]=0,4 g dl⁻¹. (○): No copper(II) chloride present; mole ratios N/Cu: (□)=1, (●)=2. Temperature: 25°C. The dotted line indicates a mole ratio N/HCl=1

UV measurements

Fig. 5 shows the increase of the absorbance at $\lambda=420\text{nm}$ of solutions of two different N/Cu mole ratios. Comparing the curves of the polymeric catalysts with those of **1** it is evident that the polymeric complexes continue to produce diphenoquinone, whereas the activity of the low molecular complexes levels off after a fast initial reaction. These curves are consistent with the yields of diphenoquinone at the end of the reaction as listed in Tab. 1.

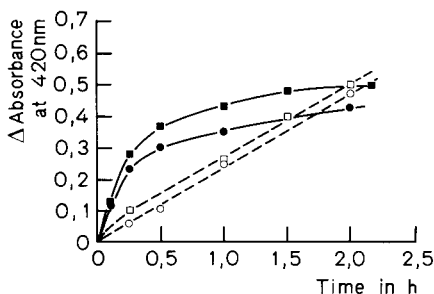


Fig. 5. Increase of absorbance at $\lambda=420\text{nm}$ during the reaction. $[\text{CuCl}_2]=1,3 \cdot 10^{-4}\text{ mol dm}^{-3}$; $[\mathbf{3}]=1,08 \cdot 10^{-4}\text{ mol dm}^{-3}$. (■): **1** + CuCl_2 with mole ratio N/Cu=2; (●): **1** + CuCl_2 with mole ratio N/Cu=1; (○): **2** + CuCl_2 with mole ratio N/Cu=1; (□): **2** + CuCl_2 with mole ratio N/Cu=2. Room temp.

Tab. 1. Yields of 2,6,2',6'-tetramethyl-1,1'-dioxo-4,4'-bicyclohexa-2,5-dienylidene (tetramethyldiphenoquinone) by oxidative coupling of **3**. $[\mathbf{3}]=1,08 \cdot 10^{-4}\text{ mol dm}^{-3}$; $[\text{CuCl}_2]_0=5 \cdot 10^{-4}\text{ mol dm}^{-3}$. Mole ratio N/Cu=2. Room temperature

Catalyst.	Conditions	Yield of diphenoquinone in %
$\text{CuCl}_2 + \mathbf{2}$	Under O_2	≈ 90
$\text{CuCl}_2 + \mathbf{2}$	Under N_2	≈ 50
$\text{CuCl}_2 + \mathbf{1}$	Under O_2	≈ 45
$\text{CuCl}_2 + \mathbf{1}$	Under N_2	≈ 30

As described in Part 1 the polymer complex with mole ratio N/Cu=2 was inactive under catalytic conditions. This meant that the solution did not absorb oxygen. However, when a sample from such a solution was taken and the optical density was measured a peak at 420nm was found. Thus, diphenoquinone has been formed, indeed. After addition of extra copper(II) chloride, dissolved in 1,2-dichlorobenzene/methanol, the reaction mixture

absorbed oxygen as yet. These experimental results point to a hindered oxygen consuming reoxidation step in the catalytic cycle for polymer complexes with high N/Cu mole ratios. Fig. 6 shows the absorption spectrum of copper complexes of **1** and **2** between 700 and 1000 nm. There are no marked differences between these spectra. However, during titration of a copper(II) chloride solution with solutions of **1** or **2** the maximum absorbance is achieved much earlier with the polymer ligands as can be seen from Fig. 7. This effect

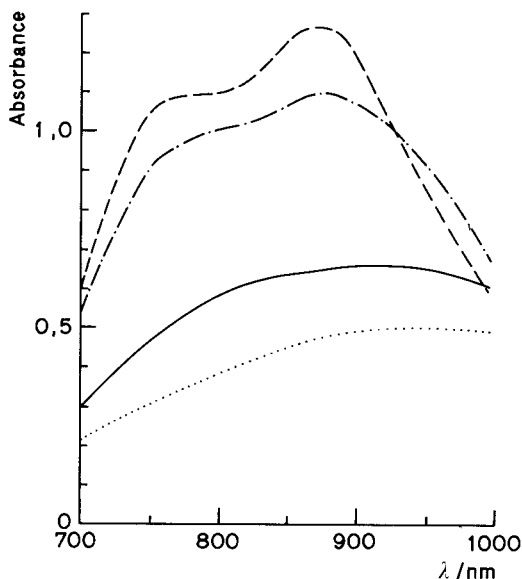


Fig. 6. Spectra of copper(II) complexes. $[CuCl_2] = 4,46 \cdot 10^{-3} \text{ mol dm}^{-3}$. (.....): copper(II) chloride; (—): $CuCl_2 + 1$, mole ratio N/Cu = 2; (- · - · -): $CuCl_2 + 1$, mole ratio N/Cu = 10; (- - - -): $CuCl_2 + 2$, mole ratio N/Cu = 2. Room temp.

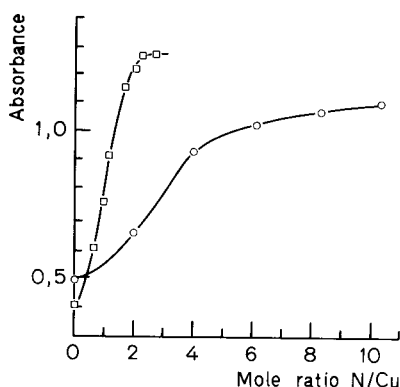


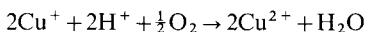
Fig. 7. Titration of a copper(II) chloride solution with **1** (○) and **2** (□). $[CuCl_2]_0 = 4,46 \cdot 10^{-3} \text{ mol dm}^{-3}$. Room temperature. Curves are not corrected for dilution

supports our view on the complexation of copper within the coils of partially dimethylaminomethylated polystyrene as described in Part 1. The complexes with at-PSII (properties see Exptl. Part) reach the maximum absorbance at mole ratio $N/Cu=2$, which indicates that the complexes contain two nitrogen per copper.

Discussion

From the results described until now it is evident that complexation of copper(II) is the most important factor governing the catalytic activity in oxidative coupling of **3**. In Part 1 this issue has been discussed in relation to the enhanced reaction rate in the range of $0 < \text{mole ratios } N/Cu < 1$ of the polymeric complexes. Extending this view now to the range of mole ratios $N/Cu \geq 1$ the following mechanism for the oxidative coupling by polymeric complexes is suggested.

Let us assume that complexation of copper(II) takes place by two amine groups. As a rule, these amine groups are located within a single polymer coil (Figs. 1 and 2), which results in strong complexation as outlined in Part 1. This means that almost all copper(II) present in solution is complexed by two amine groups. Consequently, at mole ratio $N/Cu=1$ only about half of the copper can be complexed and is located within the coils and the other half remains "uncomplexed" in solution. If we assume that complexed copper is far more active than uncomplexed copper, half of the copper has been converted into copper(I) species after reacting once with **3**. We believe that these copper(I) species are no longer attached to the amine ligands because of its low coordination ability with amine groups. Instead of copper(I) we think that protons, liberated from the phenol substrate, are attached to the polymeric ligands, which is supported by the viscometric experiments (Figs. 3 and 4). However, at mole ratio $N/Cu=1$ we still had free copper(II) in solution which can now coordinate with the amine groups by displacing protons. In this way this fraction of copper(II) becomes also active and at the same time Cu(I) and protons can react with oxygen to produce new copper(II):



On the other hand, at mole ratio $N/Cu \geq 2$ all Cu(II) can be complexed with two amine groups without leaving free Cu(II) in solution as is demon-

strated by the upper curve in Fig. 7. Thus, in the beginning of the reaction all Cu(II) can be converted into Cu(I), but reoxidation of Cu(I) to Cu(II) cannot take place since there are no uncomplexed Cu(II) ions to liberate protons needed for the reoxidation step. This explains the vanishing oxygen consumption rate at mole ratio $N/Cu \geq 2$, as found before (see Fig. 2 in Part 1). The reaction was carried out starting with copper(II) chloride instead of CuCl as usually done, because it was impossible to dissolve CuCl quantitatively. We think that CuCl dissolves in our system only after oxidation and, therefore, CuCl generated during reaction may aggregate when reoxidation is not so fast.

These considerations apply best to polymers with "high" degree of substitution by ligands. Lower degrees of substitution may result in less complete intramolecular coordination and, therefore, not all copper will be complexed at mole ratio $N/Cu=2$. Consequently, the oxygen consumption rate was not quite zero at this ratio (Part 1, Fig. 2). On the other hand, if the degree of substitution is very high, i.e. approaching 1, one could imagine for steric reasons that it is impossible for all amine groups to coordinate with copper, thus also leaving free copper in solution. Thus, there should be an optimum in the degree of substitution for the phenomena described here.

Preliminary ESR results indicated that the complexes probably contain two Cu(II), which gave no ESR signal as reported before⁶⁾. Only free copper could be detected by ESR and appeared to be present in solution with at-PSII as complexing polymer when the mole ratio $N/Cu < 2$. This strongly supports our explanation for the vanishing reaction rate at higher N/Cu mole ratios.

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