Oxidative coupling of 2,6-dimethylphenol to polyphenylene ether catalyzed by a dinuclear Cu(II) dihydroxo-diiodo complex of 2,2'-dipyridylamine

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Abstract

Some dimeric Cu(II) complexes of 2,2'-dipyridylamine (dipyam), were tested as catalysts for the oxidative coupling of 2,6-dimethylphenol (DMP) to polyphenylene ether (PPE) by dioxygen. The $Cu_2dipyam_2(OH)_2I_2 \cdot H_2O$ complex was able to assist the transformation of DMP in PPE (PPE $\geq$ 94%) under mild reaction conditions (atmospheric pressure of dioxygen; 298 K; 30 min) at very low concentration ([Cu] = 3.2×10^{-4}; [DMP]/[Cu] = 250). The diphenoquinone (DPQ), which is the side product of the reaction, could be easily maintained under 4 wt%, with a specificity PPE/DPQ $\geq$ 24. The polymerization degree of PPE could be tuned ($\bar{M}_w$ 45000–196000) by some variables of the catalytic system, as solvent medium, ligand and iodide concentrations, but primarily by using different amounts of OH$^-$ anions as co-catalyst. The conditions suitable to obtain a PPE of prefixed characteristics were statistically studied.

Keywords: 2,6-dimethylphenol oxidation; Dinuclear Cu(II)dihydroxo complexes; Homogeneous catalysis; Polyphenylene ether

1. Introduction

The study of the catalytic oxidation of phenols by dinuclear copper complexes with nitrogen containing ligands is of high interest for its correlations with the dioxygen metabolism by type III copper proteins, for example hemocyanin and tyrosinase. The oxidative coupling of 2,6-dialkylphenols presents also industrial interest since Hay's discovery [1,2] that this reaction can produce polyphenylene ethers, plastic materials of valuable technological characteristics such as chemical stability, high glass transition temperature and excellent self-extinguish properties [3]. The autoxidation of 2,6-dimethylphenol (DMP) gives poly(2,6-dimethyl-1,4-phenylenether) (PPE) and 3,3',5,5'-tetra-methyl-4,4'-diphenoquinone (DPQ) as shown in Scheme 1. One of the most important conditions to produce polymer selectively is the choice of a substrate with small substituents, but also several other factors dramatically affect ratio and quality of the final products and have to be

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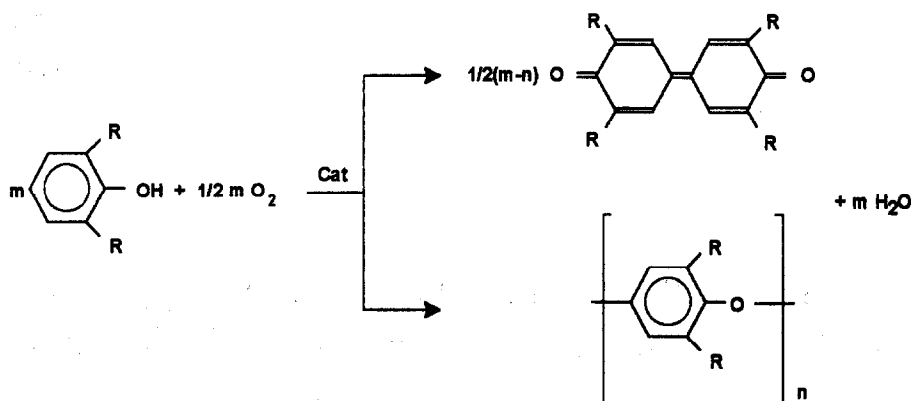
Scheme 1.

optimized to reach a satisfactory result. The two pathways of the reaction seem to be governed by an equilibrium among different catalytic species, whose formation and relative concentrations just depend on the experimental conditions [4–6]. Complexes with one [2,5,7–10], two [11,12] or more [13] copper atoms have in turn been suggested as C–O coupling catalysts.

While studying the autoxidation of 2,6-di-*tert*-butylphenol to 3,3′,5,5′-tetra-*tert*-butyl-4,4′-diphenoquinone by a variety of Cu(II) dinuclear complexes with nitrogen chelating ligands [14] and the optimization of its formation conditions [15], we had observed that some of those catalysts could also be precursors for the production of PPE from 2,6-dimethylphenol. In this paper we report a study of this reaction in the presence of a $Cu_2dipyam_2(OH)_2I_2 \cdot H_2O$ (dipyam = 2,2′-dipyridylamine) complex. In particular we considered the effects of some experimental variables on the yield and degree of polymerization of the PPE and the way to individuate reaction conditions suitable to obtain a polymer of prefixed characteristics.

2. Experimental

2.1. Synthesis of the precursor $Cu_2dipyam_2(OH)_2I_2 \cdot nH_2O$ (n = 0, 1) (I)

Dioxygen was bubbled through a suspension of 2.0 g of [Cu(dipyam)I]$_2$ [16] in 50 mL of a 1:1 water/MeOH mixture. The color of the complex turned slowly from cream to green–blue. After two hours the product was filtered off, washed repeatedly with the solvent mixture and dried under vacuum (1.78 g; dec. p.: 187–189°C). Deep-turquoise, slightly hygroscopic microcrystals were obtained from hot solutions of the above product in water/MeOH or water/acetone mixtures, after cooling to room temperature and slow evaporation of the organic solvent. Dec. p.: 190–191°C, with gas evolution. Calcd. for $C_{20}H_{20}Cu_2I_2N_6O_2$: C, 31.72; H, 2.66; Cu, 16.78; I, 33.51; N, 11.10%. Found: C, 31.9; H, 2.5; Cu, 16.6; I, 32.8; N, 11.0%. For the rough product and some of the recrystallized samples the elemental analysis was in agreement with the presence of one molecule of crystallization water.

Except for the preliminary experiments, the rough product of the above batch was used as precursor throughout this work.

2.2. General procedure

The procedure for the oxidation is described in a previous paper [14]. The substrate was added as a concentrated methanolic solution and, to obtain a better reproducibility, the addition was made all at once, although it is known that this procedure favors the formation of DPQ [6,7,9]. DMP (Aldrich, 99 wt%) was recrystallized twice (DPQ $\leq 4 \times 10^{-4}$ wt%) and dried under vacuum before use. The other chemicals

Table 1
Comparison among the activities of $Cu_2dipyam_2(OH)_2X_2 \cdot 2H_2O$ [14] precursors with different halides [a]

Halide	Total yield (%)	PPE (%)	DPQ (%)	PPE/DPQ
Cl⁻	11.1	4.4	6.7	0.7 [b]
Br⁻	61.5	52.6	8.9	5.9
I⁻	92.5	81.5	11.3	7.2

[a] Standard conditions.
[b] At such low amount of PPE the value of the PPE/DPQ ratio is highly affected by the polymer solubility, even if very poor.

were reagent grade materials used without purification. Hydroxide ions were added as methanolic KOH.

As soon as the substrate was added to the precursor solution a yellow color developed. The color turned then gradually to orange–red, sometimes also with formation of red crystals, while the precipitation of PPE began after ten minutes or more, depending on the experimental conditions.

If not differently stated the standard conditions were: $[Cu] = 3.2 \times 10^{-4}$ M; $[dipyam]/[Cu] = 2$; $[OH^-]/[Cu] = 2$; $[DMP]/[Cu] = 250$ in a 1:1 v/v mixture (25 mL) of MeOH and toluene and the autoxidation was ran on for 60 min at 298 ± 0.1 K. The reaction was then quenched by addition of 1 mL water (0.5 mL of aqueous HCl 2 M in the preliminary experiment of Tables 1 and 2 and Figs. 1 and 2) and diluted with MeOH to 50 mL to complete the precipitation of the polymer. After 30 min the PPE was filtered out, dried and weighed (A), while the DPQ was determined

Table 2
Activity of the precursor in MeOH: other solvent = 1:1 v/v [a]

Solvent	Total yield (%)	PPE (%)	DPQ (%)	$\overline{M}_w$
Toluene	93.4	79.4	14.0	94300
n-hexane [b]	85.6	79.6	9.0	33200
Chlorobenzene	77.2	58.2	19.0	133000
Acetonitrile [c]	59.5	42.9	16.6	12700
Ehtylacetate		traces	12.3	4600
Dichloroethane		traces	13.1	1400
Dioxane	no reaction			

[a] Standard conditions for the other variables.
[b] Final presence of two liquid phases.
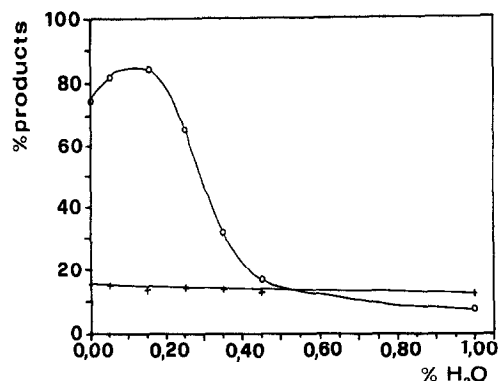[c] Colloidal liquid phase, difficult to filtrate.

Fig. 1. Effect of water content on the oxidation of DMP (standard conditions for the other variables). (○) PPE; (+) DPQ.

spectrophotometrically at 414 nm [2] in the diluted mother liquors (B). If some DPQ was included in the polymer, the latter was dissolved in $CHCl_3$ and the DPQ content found in these solutions was substracted from A and added to B to give the correct amounts of PPE and DPQ respectively. The measurements must be carried out within a hour, because the color intensity decreases in the course of time, probably as consequence of an equilibrium between DPQ and the polymeric species [17].

The percentage of conversion should be calculated on the basis of the unreacted DMP, but having not found a rapid reliable method for its determination, we calculated the reaction yield as the sum of the recovered PPE and DPQ. This value is surely less than quantitative, owing to mechanical losses in the workup procedure and to the presence of oligomeric fractions, soluble in the reaction medium.

2.3. Molecular weights measurements

The weight average molecular weight $\overline{M}_w$ and the polydispersion index D ($D = \overline{M}_w/\overline{M}_n$; $\overline{M}_n$ = number average molecular weight) of the polymers were determined by gel permeation chromatography, by a Milton Roy CM 4000

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[2] PPE does not adsorb at this wavelength and other products are not present in significant amounts.
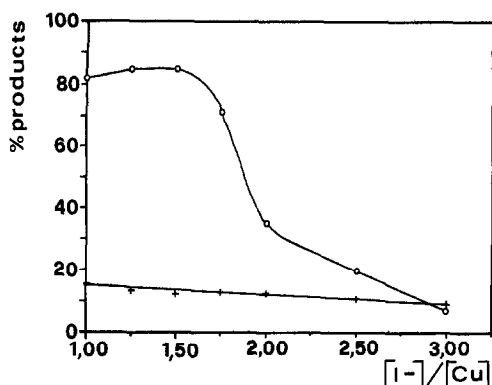
Fig. 2. Effect of iodide anion addition on the autoxidation of DMP (standard conditions for the other variables). (O) PPE; (+) DPQ.

apparatus. Columns: Chrompack Microgel-5, 10^2; 10^3; 10^4 Å (250 × 7.7 mm); eluent: $CHCl_3$; flow rate 0.5 mL/min; detection: UV, 270 nm. Calculations were made by the Spectra-Physics software program GPC/PC, using for the calibration 12 monodisperse polystyrene standards ($D \leq 1.05$) in the molecular weight range of 2.8×10^3–4.24×10^5. Dispersion corrections were not applied.

The values reported in the tables are the average of two measurements on the same polymer solution and were obtained by narrow standard ($\overline{M}_w$) or universal ($\overline{M}_w^*$) calibration methods. The Mark–Houwink constants employed for the latter method were $K = 1.20 \times 10^{-4}$ mL/g; $a = 0.76$ for the polystyrenes and $K = 4.83 \times 10^{-4}$ mL/g; $a = 0.64$ for the PPE [18].

Usually the GPC chromatograms show two not completely resolved peaks. When an approximate separate integration of the bands has been performed, the respective weight average molecular weights are reported as $\overline{M}_{w1}$ and $\overline{M}_{w2}$ and their percentages are given in parentheses.

2.4. Viscosity measurements

Intrinsic viscosities $[\eta]$ were measured in Ubbelohde dilution viscometers in chloroform solution at 298 ± 0.1 K, using the customary extrapolation of several values of the viscosity to zero concentration.

3. Results and discussion

The preliminary experiments for the polymerization of the DMP were carried out in the presence of dinuclear dihydroxo bridged complexes of Cu(II) with dipyam and halides (X = Cl^-, Br^-, I^-). Depending on the preparative conditions these complexes present a variable number of solvent molecules and assume different structural geometries. The X-ray diffraction analysis of some chloride complexes [16,19] established, for example, that halide or water can also act as a third bridging ligand between the two copper atoms (Scheme 2) and that the OH^- can be substituted by OCH_3^- group in pure methanol [16].

The reaction mechanism proposed for the homogeneous polymerization of the DMP at constant pressure of dioxygen with catalysts similar to ours is of Michaelis–Menten type (Scheme 3) [10]: the formation of an intermediate between the phenol and the catalyst is followed by a reduction of Cu(II) to Cu(I) by the substrate, which leaves then as aryloxy radical and reacts further to the final products. Cu(I) is reoxidized to Cu(II) by dioxygen.

It was claimed that the presence of halides favors the last step of the cycle, owing to formation of μ-halide dinuclear complexes [5,20–22]. Our results underline that also the kind of halide affects heavily the catalytic activity. The iodo complexes, which are usually not taken into account in the literature, gave much better results than the corresponding chloro and bromo derivatives (Table 1) and therefore we concentrated our interest on these compounds.

3.1. The catalytic system

The iodo complexes could be prepared either by autoxidation of the $[Cu(dipyam)I]_2$ complex
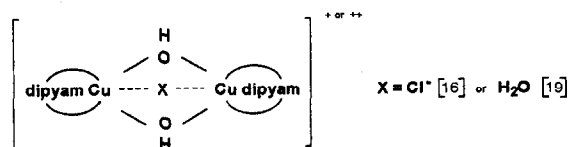
Scheme 2.

Table 3
Effect of solvent composition on the polymerization [a]

MeOH/toluene (v/v)	Total yield (%)	PPE (%)	DPQ (%)	PPE/DPQ	$\bar{M}_w$	$\bar{M}_{w1}$ (%)	$\bar{M}_{w2}$ (%)	D
0.60 [b]	86.1	71.3	14.8	4.8	77900	335000 (13.0)	39500 (87.0)	2.74
0.80	92.4	77.0	15.4	5.0	119800	416000 (17.6)	56900 (82.4)	3.17
1.00	93.4	80.4	13.0	6.2	123200	430000 (18.5)	53200 (81.4)	4.02
1.20	95.5	82.3	13.2	6.2	129700	435500 (20.7)	50700 (79.3)	4.11
1.40	84.7	72.9	11.8	6.2	134000	442000 (22.1)	47000 (77.9)	4.16

[a] Standard conditions for the other variables.
[b] Colloidal liquid phase, difficult to filtrate.

or by treatment of other dinuclear dihydroxo Cu(II) derivatives with a KI excess [14]. Among the different complexes obtained by starting from the same reagents in the same ratio but in different solvent media [23] we chose as precursor for this study the $Cu_2dipyam_2(OH)_2I_2 \cdot H_2O$ complex (I), which is the most easy to handle.

In agreement with the proposed formula the IR spectrum of I shows a medium absorption band [3] at 3460 cm^{-1}, attributable to bridging OH$^-$ stretches [19] (see, for example, Ref. [24]) and a weaker band at 502 cm^{-1}, which is in the range of frequencies usually assigned to ν_{asym}(Cu–O) (see, for example, Ref. [25]). The powder EPR spectrum is practically silent at room temperature.

In the polymerization experiments I was used as a methanol solution. In this solvent the complex turns to another species (II) isolated as a silky pale blue powder, in which the OH$^-$ are substituted by CH$_3$O$^-$ groups: the IR spectrum shows no more the 3460 cm^{-1} band, while a new peak appears in the range of bridging alkoxides absorption [26], at 1035 cm^{-1}. The Cu–O peak broadened and shifted to 480 cm^{-1}. II hydrolized slowly in the air, reforming the parent complex and releasing two/three molecules of MeOH, which could be identified by GC in DMF.

Complex II did not change further in a 1:1 MeOH/toluene mixture, which is the solvent medium utilized for the catalysis.

As found for numerous other precursors the above complexes display significant activities for the oxidative C–O coupling only after addition of free ligand and OH$^-$ anions. Under the catalytic standard conditions apparently all the complexes of the iodo series turn to the same species, since all exhibit the same visible spectrum with a broad maximum at about 567 nm and gave similar polymerization results.

From the catalytic system we were so far unable to isolate definite complexes, except for [Cu(dipyam)$_2$I$_2$] [23] and [Cu(dipyam)CO$_3$ · 3H$_2$O]$_n$ [27], which clearly are decomposition side-products.

3.2. Choice of the solvent

Literature data indicate apolar solvents as the most suitable for the oxidative coupling of DMP
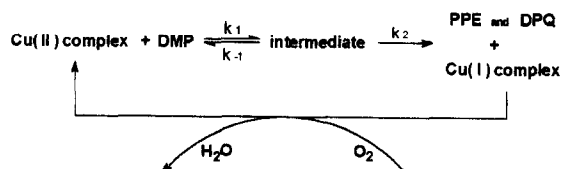
Scheme 3.

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[3] This band is rather sharp in the anhydrous complex, but broadens asymmetrically towards lower frequencies in the presence of crystallization water.

Table 4
Effect of dipyam addition on the polymerization [a]

[Dipyam]/[Cu]	Total yield (%)	PPE (%)	DPQ (%)	PPE/DPQ	$\overline{M}_w$	$\overline{M}_{w1}$ (%)	$\overline{M}_{w2}$ (%)	D
1	63.8	49.3	14.5	3.4	34500	279000 (2.4)	28200 (97.6)	1.69
2	93.7	80.5	13.2	6.1	93100	410800 (14.8)	38500 (85.2)	4.02
3	95.2	81.7	13.5	6.0	144500	428000 (24.1)	55200 (75.9)	3.70
4 [b]	93.7	79.7	14.0	5.7	105000	399500 (13.9)	59400 (86.1)	2.80
5 [b]	71.8	58.5	13.1	4.4	44200	268500 (5.9)	30500 (94.1)	2.10

[a] Standard conditions for the other variables.
[b] Colloidal liquid phase, difficult to filtrate.

[12], however, in our case, the presence of MeOH is necessary for the complex solubilization. We tried hence for the reaction a series of 1:1 mixtures of MeOH and various organic solvents (Table 2) and, on the basis of conversion factor, PPE/DPQ ratio and $\overline{M}_w$ of the polymer, we selected as solvent the MeOH/toluene mixture [4]. A variation of its composition affected mainly the polymerization degree (Table 3).

In the range of the experimented conditions the conversion yield was better in commercial than in anhydrous solvents, however the yields decreased rapidly at water concentrations > 0.2 wt% (Fig. 1). Although water does not destroy the complex, it can modify its structure [16], and this variation could be responsible for the precursor deactivation. The water content does not affect, instead, the formation of DPQ (Fig. 1).

3.3. Effect of an excess of iodide

The type and concentration of the counterions in the solution are often determining for the activity of the catalyst [5,21].

In the case of our precursor the polymeriza-

tion reaction was slightly improved by a low addition a iodide, but a higher amount of halide inhibited it severely, till suppressing the C–O coupling almost completely at a $[I^-]/[Cu]$ ratio $= 3$ (Fig. 2). A strong excess of iodide probably inhibits the formation of OH^- bridges, also in the presence of a $[OH^-]/[Cu]$ ratio of 2, destroying the catalytic activity. Cu(II) dipyam complexes with halide as only other ligand are indeed inactive.

3.4. Effect of dipyam addition

Until a [dipyam]/[Cu] ratio of about 3 the ligand addition improved the oxidation of DMP and the selective formation of polymer (Table 4). At higher ratios the PPE yield decreased and the mixture became also difficult to filtrate. Probably the addition of a moderate excess of ligand leads to the formation of modified species, more active towards the polymerization than to the dimer production, which are then destroyed by a high amount of dipyam. We are trying to verify this hypothesis.

3.5. Effect of $[OH^-]/[Cu]$ ratio

The addition of OH^- anions to the reaction mixture caused the most important effects on the DMP polymerization. The rate and the selectivity of the oxidation were largely improved by an increase of basicity, while the favorable

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[4] n-hexane was excluded because of the incomplete miscibility of the final mixture. Alcohols with higher molecular weight, such as iso-propanol and n-butanol, are poor solvents for the Cu(II) complex.

effect on PPE yield and polymerization degree reached a maximum at $[OH^-]/[Cu]$ ratios of about 8 and 3 respectively (Table 5). An OH^- excess, in the range $3 \leq [OH^-]/[Cu] \leq 6$, improved also the physical characteristics of the polymer, which was recovered as a white microcrystalline powder (DPQ content ≤ 0.02 wt%), while traces of a yellow product, insoluble in $CHCl_3$, were formed at higher concentrations of the base.

A strong basic reaction medium, besides to deprotonate the weakly-coordinating phenol to its more reactive anion favoring its coordination to copper [7,22,28], should also help to reintroduce bridging OH^- groups in our catalysts once the reoxidation has occurred. An excess of basicity, however, can lead to a partial decomposition of the catalyst, with formation of inactive side-products of the type $Cu_2(OH)_3X$ [21].

Also for our precursor better results were found when OH^- was added to the substrate rather than to the catalytic system (Table 5).

3.6. C–C coupling

Formation of small amounts of the undesired DPQ cannot be avoided [12,28] also with our precursor, the behavior of which towards the C–C coupling is qualitatively similar to that observed for the majority of the catalytic systems already described in the literature.

The DPQ yield depends on the reaction medium (Table 2). In the range of the experimental conditions taken into account the DPQ production decreased by an increase of basicity (Table 5), while it was almost unaffected by a [dipyam]/[Cu] ratio higher than 2 (Table 4) and, under these conditions, by the initial concentration of the substrate (Table 6).

We did not study the effect of the temperature, an increase of which is known to slightly favor the C–C coupling [6,12].

Once formed, the DPQ undergoes side reactions and a marked decrease of its amount was observed when the reaction time was prolonged

Table 5
Effect of base addition on the polymerization [a]

$[OH^-]/[Cu]$	Total yield (%)	PPE (%)	DPQ (%)	PPE/DPQ	$\overline{M}_w$	$\overline{M}_{w1}$	D
1.0	9.4		9.4				
2.0 [b]	90.5	79.8	10.7	7.5	68900	482200 (5.0)	2.38
2.0 [c]	94.2	83.7	10.5	8.0	74100	501600 (5.0)	2.50
3.0 [b]	96.6	89.7	6.9	13.0	93500	593600 (4.1)	2.53
3.0 [c]	98.8	92.5	6.3	14.7	92600	583200 (3.8)	2.45
5.0 [b]	97.2	93.0	4.2	22.1	84800	621100 (1.6)	2.20
5.0 [c]	98.5	93.4	4.1	22.8	79200	624400 (1.1)	2.26
7.5 [b]	96.8	93.4	3.5	26.7	71300	652500 (0.5)	2.06
7.5 [c]	98.1	94.8	3.3	28.7	65100	627000 (0.4)	1.96
10.0 [b]	94.7	91.4	3.3	27.7	60800	572000 (0.3)	1.80
10.0 [c]	98.8	95.7	3.1	30.9	73300	619600 (0.4)	1.94

[a] Reaction time: 30 min.
[b] OH^- addition made by the standard procedure.
[c] Base addition to the substrate, instead of to the complex solution.

Table 6
Effect of [DMP]/[Cu] ratio on the autoxidation reaction [a]

$\frac{[DMP]}{[Cu]}$	Total yield (%)	PPE (%)	DPQ (%)	$\bar{M}_w$	$\bar{M}_{w1}$ (%)	D
100	98.1	93.8	4.3	120100	675800 (3.7)	2.61
175	97.8	93.4	4.4	81000	637300 (1.5)	2.23
250	97.0	92.7	4.3	69000	605700 (1.1)	2.01
375	92.0	87.8	4.2	46900	494400 (0.3)	1.57
500	85.7	81.5	4.2	38700	a single peak	1.44
500 [b]	96.0	91.7	4.3	557700	587900 (0.8)	1.81

[a] Reaction time: 30 min; MeOH/toluene = 1; [dipyam]/[Cu] = 3; [OH$^-$]/[Cu] = 5.
[b] Reaction time: 60 min.

beyond the complete conversion of the substrate (Table 7). Table 7 confirms also that DPQ is mainly formed in the initial stage of the reaction, like observed for other catalytic systems based on copper complexes [6–10,28,29].

3.7. Degree of polymerization

The degree of polymerization of PPE was found to depend on the solvent (see for example the high $\bar{M}_w$ in chlorobenzene) but, in the same medium, it was correlated with the conversion stage, in turn depending, for the same reaction time, on the other variables (Table 6).

For close PPE yields the formation of a polymer of high mass was favored by moderate additions of dipyam, I$^-$ and OH$^-$ to the precursor solutions. An increase of the methanol fraction in the solvent decreased instead the polymerization degree: this could be due to the lower solubility of the PPE in the new medium, causing the precipitation already of short chains of polyphenylene ether, which are hence substracted to a further growth process [30]. High [OH$^-$]/[Cu] ratios also decreased the molecular weight of the PPE, owing to the fast competitive starting of a lot of oligopolymeric chains, which cannot achieve a high polymerization

Table 7
Effect of time on the oxidation reaction [a]

Run	Min	Total yield (%)	PPE (%)	DPQ (%)	$\bar{M}_w$	$\bar{M}_{w1}$ (%)	D	$[\eta]$ dL g^{-1}
A [b]	15	67.1	60.3	6.8	36300	395900 (0.5)	1.61	0.45
	30	95.6	88.7	6.9	75300	550700 (3.2)	2.44	0.56
	120	97.4	92.3	5.1	195900	637500 (19.8)	4.38	0.70
B [c]	15	88.0	83.4	4.6	37400	421300 (0.7)	1.71	0.41
	30	98.0	93.7	4.3	77400	573500 (2.6)	2.64	0.55
	120	97.2	94.7	2.5	1179006	543700 (10.2)	3.65	0.60
C [d]	15	86.2	82.4	3.8	29800	378000 (0.4)	1.66	0.27
	30	98.9	95.3	3.6	45300	562100 (0.8)	2.10	0.37
	120	96.9	94.9	2.0	77000	585400 (5.1)	3.25	0.47

[a] [DMP]/[Cu] = 250.
[b] MeOH/toluene = 1; [dipyam]/[Cu] 2; [OH$^-$]/[Cu] = 3.
[c] MeOH/toluene = 1.5; [dipyam]/[Cu] = 3; [OH$^-$]/[Cu] = 5.
[d] MeOH/toluene = 2; [dipyam]/[Cu] = 4; [OH$^-$]/[Cu] = 7.

degree before the complete conversion of the substrate.

The presence in the chromatogram of bands of rather different average molecular weights, observed sometimes also at low conversion stages, excludes a simple stepwise addition of monomer units in the polymerization process: according to the literature the mechanism of the oxidation should be a rare case of reactive intermediate polycondensation [31]. The homogeneity of the PPE decreased by prolonging the reaction time after the total conversion of the substrate and was dramatically affected by the experimental conditions (Fig. 3).

There is a reasonable agreement between the weight average molecular weights data calculated by the two calibration methods and between the calculated and measured intrinsic viscosities. The differences depend, at least in part, on the shapes of the chromatographic curves, which are affected mainly by the solvent composition, while little effect of the other variables is observed (Fig. 4).

3.8. Optimization of the autoxidation reaction of DMP to PPE by experimental design and the response surface methodology

As we reported in a previous paper [15] a system characterized by several input variables and several response outputs can be described by a mathematical simulation, whose elaboration allows also an optimization of the experimental conditions.

At first we considered a simple linear model:

$$y = b_0 + b_1 x_1 + b_2 x_2 + \ldots + b_k x_k + \epsilon$$

where x_i are the variables, ϵ represents the error and y the response. The unknown coefficients b_i are obtained by regression using the least square method [32]. The absolute value of b_i shows the entity, while the sign indicates the positive or negative influence of the single variable x_i on the response y. To get these preliminary informations we used a two-level factorial experimental design.

To better evidentiate the minor effects of some parameters, in a first series of experiments the OH^- concentration, which is the most important parameter of the reaction, was kept constant ($[OH^-]/[Cu] = 3$), taking into account the variables: $MeOH/toluene = 1-2$, $[dipyam]/[Cu] = 2-6$ and $[I^-]/[Cu] = 1-2$. As can be inferred from the absolute value of the coefficients, in the selected experimental region the variables $[dipyam]/[Cu]$ and $MeOH/toluene$ have a comparable influence, while $[I^-]/[Cu]$ has a scarcely important effect on selectivity, $\overline{M}_w$ and D. On the basis of these results a second series of experiments was run to find out the most favorable conditions of polymerization, including the $[OH^-]/[Cu]$ and neglecting the $[I^-]/[Cu]$ variable (Table 8). What we tried to optimize, at a practically total conversion,
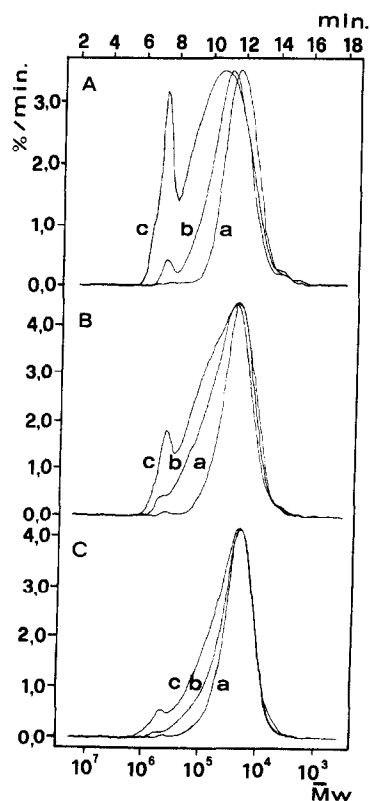

Fig. 3. Variation of the distribution of the molecular weights by prolonging the reaction time beyond the total conversion of the substrate. The curves correspond to the samples of Table 7: (a) 15 min; (b) 30 min; (c) 120 min.
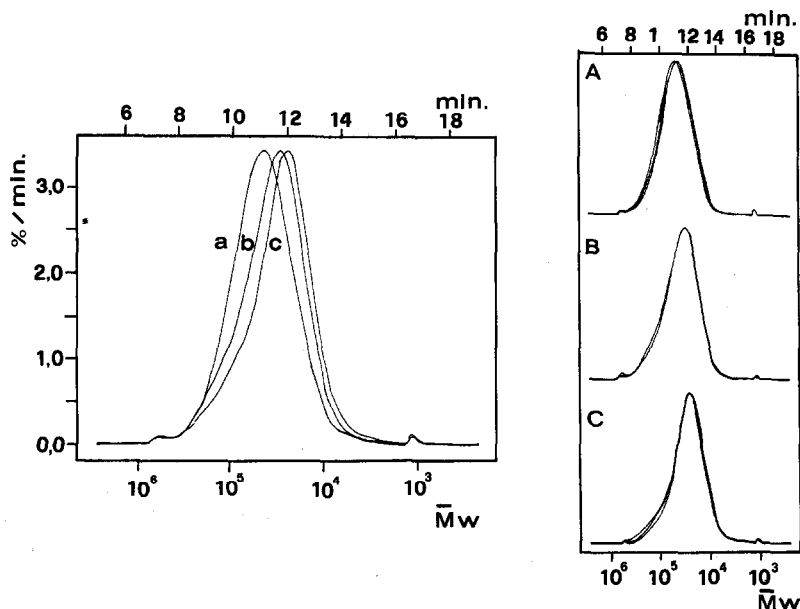
Fig. 4. Influence of the solvent composition, [dipyam]/[Cu] and [OH$^-$]/[Cu] ratios on the shape of the distribution curves of the $\overline{M}_w$. (a, b, c) MeOH/toluene = 1, 1.5, 2, respectively; other variables: [dipyam]/[Cu] = 3, [OH$^-$]/[Cu] = 6. (A, B, C) MeOH/toluene = 1, 1.5, 2, respectively; other variables coupled as follows: [dipyam]/[Cu] = 2, [OH$^-$]/[Cu] = 4; [dipyam]/[Cu] = 2, [OH$^-$]/[Cu] = 8; [dipyam]/[Cu] = 3, [OH$^-$]/[Cu] = 6; [dipyam]/[Cu] = 4, [OH$^-$]/[Cu] = 8.

was the $\overline{M}_w$, together with characteristics of high selectivity (PPE/DPQ $\geq$ 22.0), low D ($\leq$ 2.20) and intrinsic viscosity suitable for industrial processing ([η] $\leq$ 0.5 dL/g) [5]. To get this purpose, we selected a quadratic (three-level) model with interaction:

$$y = b_0 + b_1 x_1 + b_2 x_2 + b_3 x_3 + b_{11} x_1^2 + b_{12} x_1 x_2$$
$$+ b_{13} x_1 x_3 + b_{22} x_2^2 + b_{23} x_2 x_3 + b_{33} x_3^2$$
$$+ b_{123} x_1 x_2 x_3 \qquad (1)$$

for the response $\overline{M}_w$ and a linear model:

$$y = b_0 + b_1 x_1 + b_2 x_2 + b_3 x_3 \qquad (2)$$

for the responses PPE/DPQ, [η] and D.

To reduce the number of experiments (3^n trials) we applied the D-optimal criterion [33,34], which guarantees the efficiency and reliability of the estimated parameters without loss of information. The research of the optimal

point inside the prefixed experimental region was made by using the Box algorithm [35], which, by using the simplex technique, allows to find out the maximum of the objective function subject to inequality constraints. The coefficients of the objective function (1) and that of the constraints functions (2) were determined by regression analysis (Table 9). The results were:

$$x_1 = \text{MeOH/toluene} = 1.1$$

$$x_2 = [\text{dipyam}]/[\text{Cu}] = 1.7$$

$$x_3 = [\text{OH}^-]/[\text{Cu}] = 7.0$$

In three tests performed by using experimental conditions close to those calculated, we obtained the data summarized in Table 10. The prefixed characteristics of the polymer are respected.

3.9. Comparison with other catalytic systems

A significative comparison between the performances of our precursor and those of other catalysts is possible only with the results of the

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[5] An Aldrich commercial sample, processed with our methods, gave $\overline{M}_w$ 44200 ($\overline{M}_w1 \approx 0$); D 2.40; [η] 0.470.

Table 8
Interactive effect of some variables on PPE production

x_1 [a]	x_2 [b]	x_3 [c]	Total yield (%)	PPE (%)	DPQ (%)	PPE/DPQ (%)
1.0	2.0	4.0	94.9	89.8	5.1	17.6
1.0	2.0	6.0	95.4	91.1	4.3	21.2
1.0	2.0	8.0	96.6	93.2	3.4	27.4
1.0	3.0	6.0	96.5	92.5	4.0	23.1
1.0	3.0	8.0	97.6	94.1	3.5	26.9
1.0	4.0	8.0	97.7	94.3	3.4	27.7
1.5	2.0	6.0	98.5	94.4	4.1	23.0
1.5	3.0	4.0	96.8	91.8	5.0	18.4
1.5	3.0	6.0	97.9	94.0	3.9	24.1
1.5	4.0	8.0	97.5	94.0	3.5	26.9
2.0	2.0	4.0	95.7	90.7	5.0	18.1
2.0	2.0	8.0	96.1	92.6	3.5	26.5
2.0	4.0	4.0	98.1	93.2	4.9	19.0
2.0	4.0	8.0	98.7	95.4	9.9	28.9

x_1 [a]	x_2 [b]	x_3 [c]	$\overline{M}_w$ ($\overline{M}_{w1}$%)	D	$\overline{M}_w$ *	D *	$[\eta]$ *	$[\eta]$
1.0	2	4	59900 (0.8)	1.82	59000	2.00	0.498	0.472
1.0	2	6	52200 (0.8)	1.84	50900	2.02	0.458	0.461
1.0	2	8	60500 (0.4)	1.86	59500	2.05	0.501	0.468
1.0	3	6	61800 (0.7)	1.86	60800	2.05	0.510	0.533
1.0	3	8	62000 (0.6)	1.87	61100	2.06	0.510	0.524
1.0	4	8	66900 (0.9)	2.00	66200	2.22	0.530	0.504
1.5	2	6	54700 (0.7)	2.07	53800	2.32	0.459	0.483
1.5	3	4	59700 (1.0)	2.13	59200	2.40	0.484	0.495
1.5	3	6	56900 (0.7)	2.06	56100	2.31	0.470	0.470
1.5	4	8	56900 (0.7)	2.12	56200	2.38	0.470	0.484
2.0	2	4	44700 (0.6)	1.94	43600	2.15	0.402	0.392
2.0	2	8	38100 (0.2)	1.83	36400	2.02	0.363	0.382
2.0	4	4	50600 (0.9)	2.11	50200	2.40	0.430	0.404
2.0	4	8	47100 (0.5)	2.09	46400	2.36	0.410	0.427

[a] x_1 = MeOH/toluene.
[b] x_2 = [dipyam]/[Cu].
[c] x_3 = [OH⁻]/[Cu].

Dutch scientists, who operated under experimental conditions not too far from ours. The best among their catalysts, the $CuCl_2/N,N,N',N'$-tetramethylethylenediamine system [12,21,22,28], seems to require a [Cu]/[substrate] ratio twenty times higher to give a DMP conversion comparable with that obtained in the presence of the

Table 9
Coefficients b_i of the square model for $\overline{M}_w$ and of linear model for PPE/DPQ, [η] and D estimated from the data of Table 8 by the least squares method referred to the coded variables

Coefficients	$\overline{M}_w \times 10^{-3}$	PPE/DPQ	[η]	D
b_0	55.18	23.49	0.46	2.20
b_1	−25.52	0.76	−0.15	0.21
b_2	12.38	1.61	0.06	0.38
b_3	−3.70	13.94	−0.01	−0.13
b_{11}	−7.15			
b_{12}	2.05			
b_{13}	−2.35			
b_{22}	−0.10			
b_{23}	−2.07			
b_{33}	4.31			
b_{123}	2.82			

$Cu_2dipyam_2(OH)_2I_2 \cdot H_2O$ complex. The selectivity observed is instead better: the DPQ content was usually about 3.1 ± 0.6 wt% [28] and could be lowered under 1 wt% adding the DMP to the reacting system in small portions [8,21]. The initial presence of PPE oligomers in the substrate allowed to further depress the DPQ production [7–10]. The last two techniques, which we have not experimented so far, should, however, improve also the selectivity of our system.

No comparison is possible for the degree of polymerization and polydispersivity index of the PPE, because the few data present in the above studies refer to repeatedly recrystallized samples [25,32] and not to rough products as in our case.

We wish at this point to emphasize also that, while we obtained a polymer of good quality,

not all the catalytic systems are suitable to synthesize high purity PPE [36,37].

4. Conclusions

The $Cu_2dipyam_2(OH)_2I_2 \cdot H_2O$ complex employed as precursor in the homogeneous catalytic oxidation of DMP, allows to obtain an almost pure PPE in high yield, under mild reaction conditions ($p_{O_2} = 1$ atm, temperature $\leq 25°C$), with short reaction times and at very low catalyst concentrations. Its performance can be considered satisfactory if compared with that of similar catalytic systems of the literature.

The precursor is not expensive and the polymerization can be carried out in common commercial solvents. Conversion, selectivity, polymerization and polydispersion degree of the product can be controlled by variables such as solvent medium, [dipyam]/[Cu], [I$^-$]/[Cu] and [OH$^-$]/[Cu] ratios and reaction time. Determining for the polymerization is the addition of OH$^-$, which acts as a co-catalyst in the process, but an excess of ligand in the field [dipyam]/[Cu] = 2–3 is also relevant to obtain a highly active catalyst, selective for the polymer formation. A suitable solvent is a mixture of MeOH/toluene 1–1.5:1 v/v.

The optimization of the working conditions to obtain PPE of prefixed characteristics is possible on the basis of a statistical approach, handling the analytical data by experimental design and response surface methodology.

Table 10
Results obtained from experiments performed under the optimized conditions [a]

Total yield (%)	PPE (%)	DPQ%	PPE/DPQ	$\overline{M}_w$ ($\overline{M}_{w1}$%)	D	$\overline{M}_w$ *	D *	[η] *	[η]
98.0	94.1	3.9	24.1	58700 (0.8)	1.96	57800	2.18	0.488	0.49
98.3	94.4	3.9	24.2	29800 (0.9)	2.03	59200	2.26	0.489	0.47
97.7	93.8	3.9	24.0	58100 (0.6)	1.88	57000	2.07	0.486	0.48

[a] Reaction time: 25 min; MeOH/toluene = 1.1; [dipyam][Cu] = 1.7; [OH$^-$]/[Cu] = 7.0.

Acknowledgements

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