

A Simple and Selective Biphasic Catalytic System for the Oxidative Polymerization of 2,6-Dimethylphenol

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In honour of Roger A. Sheldon on the occasion of his 60th birthday.

Abstract: Poly(2,6-dimethyl-1,4-phenylene ether) (PPE) is widely used in high-performance engineering thermoplastics and thus, it is economically attractive. An effective catalytic procedure has been developed, consisting of a toluene/water solvent mixture in which the oxidative coupling of 2,6-

dimethylphenol (DMP) is performed. This biphasic system allows an easy separation of the polymer from the copper catalyst.

Keywords: biphasic catalysis; copper; polymers; solvent effects; water chemistry

Introduction

Since its discovery in 1959,^[1] poly(2,6-dimethyl-1,4-phenylene ether) (PPE) has become one of the most widely used engineering thermoplastics with a total sale worldwide approaching 1 billion U.S. dollars.^[2] PPE is obtained by the copper-catalyzed oxidative coupling of 2,6-dimethylphenol (DMP) (Scheme 1) which leads to the desired polymer, but also to the unwanted 4-(3,5-dimethyl-4-oxo-2,5-cyclohexadienylidene)-2,6-dimethyl-2,5-cyclohexadienone (DPQ). This polymerization has been extensively studied^[3] but the mechanism is not yet clarified in detail.^[4] The industrial challenge is to find a very active, selective, and inexpensive catalytic system allowing the formation of high-molecular-weight polymers. Furthermore, the isolation of the polymer, as well as the recycling of the nitrogen-containing ligand, the

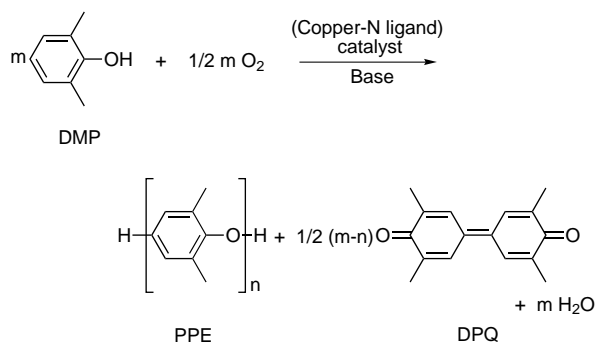
copper salt, and the solvent should not be a difficult and costly procedure.

A solution to this challenge could be the use of an organic solvent/water biphasic system with the polymer soluble in the organic phase and the copper complex in the water phase. Unfortunately, it has been shown that the water produced during the course of the reaction leads to catalyst poisoning, due to hydrolysis.^[5] Drying agents are necessary for the polymerization to continue, which is an industrially unattractive feature. Some recent publications describe the biphasic synthesis of PPE using high aqueous ammonia concentrations and an emulsifier,^[6] or high aqueous sodium hydroxide concentrations and a phase-transfer agent.^[7] Despite their scientific significance, it seems unlikely that such procedures are applicable in industry, as drastic basic conditions and additives are required.

In this paper, a novel and effective biphasic catalytic system is presented. It consists of a toluene/water solvent mixture in which the oxidative coupling of DMP is performed.

Results and Discussion

The copper catalyst, which is obtained from $\text{Cu}(\text{NO}_3)_2 \cdot 3 \text{H}_2\text{O}$ and 1-methylimidazole, is soluble in water, while DMP, and later on PPE, are soluble in toluene. Neither an emulsifier, nor a phase-transfer agent is needed and only a 6.67 mM solution of sodium methoxide is employed. These experimental conditions allow the formation of high-molecular-weight PPE, up to 86,600 Da. Several experiments have been performed



Scheme 1. Polymerization of DMP by copper-catalyzed oxidative coupling.

Table 1. Water effect on polymerizations of DMP using a biphasic catalytic system.

Entry	Ligand ^[a]	MeONa ^[b]	T [°C]	Atmosphere	H ₂ O in Toluene [%]	Conv [%] ^[c]	T ^[d]	TON ^[e]	R ₀ ^[f]	M _w ^[g]
1	30 Meim	2	25	O ₂	6.7	100	29	60	14	33,300
2	30 Meim	2	25	O ₂	13.3	99	31	59	11	20,000
3	30 Meim	2	25	O ₂	20.0	100	33	60	11	16,700
4	30 Meim	2	25	O ₂	26.7	98	43	59	11	27,800
5	30 Meim	2	25	O ₂	33.3	100	32	60	15	86,600
6	30 Meim	2	25	O ₂	33.3	99	39	59	17	86,600
7	30 Meim	2	25	O ₂	40.0	95	38	57	17	70,000
8	30 Meim	2	25	O ₂	50.0	100	31	60	13	21,200
9	30 Meim	2	25	O ₂	60.0	100	14	60	20	40,300
10	30 Meim	2	25	O ₂	60.0	100	17	60	18	53,000
11	30 Meim	2	25	O ₂	70.0	100	16	60	19	46,600
12	30 Meim	2	25	O ₂	70.0	100	16	60	21	48,600
13	30 Meim	2	25	O ₂	80.0	100	21	60	14	37,400
14	30 Meim	2	25	O ₂	87.0	100	15	60	25	47,200
15	30 Meim	2	25	O ₂	90.0	100	19	60	19	54,400
16	30 Meim	2	25	O ₂	100	84	1.8 h	50	8	No PPE

^[a] Units = equiv. per copper. Meim = 1-methylimidazole.

^[b] Units = equiv. per copper.

^[c] The conversion of DMP was based on the amount of dioxygen absorbed in this time. Selectivity in PPE was always found to be over 98%.

^[d] Units = minutes unless otherwise stated.

^[e] TON = turn-over number = moles of DMP converted per mole of copper.

^[f] Initial dioxygen-uptake rate. Units = 10⁻⁵ mol L⁻¹ s⁻¹.

^[g] Molecular weight of PPE in Dalton, measured with size exclusion chromatography.

to appraise the influence of different reaction parameters, like water amount, quantity of base, DMP to copper ratio, and equivalents of ligand, on the reaction rate and the polymer molecular weight (Tables 1 and 2).

The amount of water (Table 1) does not greatly affect the activity, but has an important effect on the molecular weight. High values are only reached when, at least, 33% water is used. It appears that a certain volume of water (30 to 40%) is essential to obtain a good emulsion and, thus, an ideal contact between the monomer and the catalyst. This is confirmed by the experiments carried out with only 4 equivalents of ligand (Table 2, entries 8 and 9). In these trials, no emulsion formation at all is observed and the molecular weights are only 3,100 Da and 4,400 Da respectively. The polymerizations are reproducible (Table 1, entries 5 and 6, 9 and 10, and 11 and 12). The influence of the variation in the amount of base added is significant (Table 2, entries 1 to 4). One and a half equivalents of base per copper lead to a molecular weight of 24,300 Da, whereas two equivalents of base give a molecular weight of 86,600 Da. A further increase of base equivalents decreases the molecular weight to a value nearby 50,000 Da to 55,500 Da. It is obvious that the optimal quantity of base lies around two equivalents per copper. A similar result has already been reported with the same catalyst in a toluene/methanol solvent mixture.^[8] Tests mentioned so far have been realized working with a DMP/Cu ratio of 60 to 1. Higher ratios (Table 2, entries 5 and 6) also render

satisfactory reaction rates and polymer molecular weights. As expected, using air instead of a pure dioxygen atmosphere (Table 2, entries 2 and 7) induces a drop in the reaction rate, illustrating the importance of the rapid reoxidation of Cu(I) species.

The copper/Meim ratio impact on the polymerization is rather dramatic (Table 2, entries 2 and 9). Not only the rates but also the molecular weights are extremely inferior with small Meim to copper ratios. When four equivalents, which is the maximal number of ligands coordinated to the copper atom, of Meim are utilized, no emulsion is observed. It seems therefore, that Meim plays also a role in the formation of the emulsion due to its solubility both in water and in toluene. This emulsion is obviously essential to attain elevated polymerization rates and high molecular weights. The presence of one additional methyl group on position 2 of the imidazole derivative (Dmiz, Table 2, entries 2 and 10) leads to shorter polymer chains.

Conclusion

A new catalytic system has been developed with great potentials, as it leads to high molecular weight PPE and as it permits an easy separation of the polymer from the catalyst (see Experimental section). These preliminary results clearly indicate that the polymerization rate and the polymer chain length, can be further improved and

Table 2. Polymerizations of DMP: Influence of several reaction parameters.

Entry	Ligand ^[a]	MeONa ^[b]	T [°C]	Atmosphere	H ₂ O in Toluene [%]	Conv [%] ^[c]	T ^[d]	TON ^[e]	R ₀ ^[f]	M _w ^[g]
1	30 Meim	1.5	25	O ₂	33.3	100	33	60	13	24,300
2	30 Meim	2	25	O ₂	33.3	100	32	60	15	86,600
3	30 Meim	2.5	25	O ₂	33.3	100	26	60	15	50,000
4	30 Meim	3	25	O ₂	33.3	100	23	60	17	55,500
5	30 Meim	2	25	O ₂	33.3	100	21	120	12	61,000
6	30 Meim	2	25	O ₂	33.3	100	39	200	11	57,700
7	30 Meim	2	25	Air	33.3	100	47	60	11	68,200
8	4 Meim	2	25	Air	33.3	71	4.5 h	43	0.5	3,100
9	4 Meim	2	25	O ₂	33.3	85	4.5 h	51	0.7	4,400
10	30 Dmiz	2	25	O ₂	33.3	100	23	60	17	22,200

^[a] Units = equiv. per copper. Meim = 1-methylimidazole; Dmiz = 1,2-dimethylimidazole.

^[b] Units = equiv. per copper.

^[c] The conversion of DMP was based on the amount of dioxygen absorbed in this time. Selectivity in PPE was always found to be over 98%.

^[d] Units = minutes unless otherwise stated.

^[e] TON = turn-over number = moles of DMP converted per mole of copper.

^[f] Initial dioxygen-uptake rate. Units = 10⁻⁵ mol L⁻¹ s⁻¹.

^[g] Molecular weight of PPE in Dalton, measured with size exclusion chromatography.

controlled by modifying the reaction parameters, like water amount, quantity of added base, equivalents of ligand and ligand structure.

Experimental Section

General Remarks

All reagents were commercially available compounds and were used as received except that 2,6-dimethylphenol (DMP) was recrystallized from *n*-hexane. Molecular weight distributions were determined by size exclusion chromatography (SEC). 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 (HPLC grade) with a flow of 1 mL min⁻¹. The concentration was 10 mg mL⁻¹; sample load was 100 µL.

Biphasic Polymerization of 2,6-Dimethylphenol

A typical catalyst solution was prepared by dissolving, in a 10-mL volumetric flask, 24.2 mg (0.1 mmol) of Cu(NO₃)₂ · 3 H₂O in 5 mL of distilled water, adding 0.24 mL (3.0 mmol) of 1-methylimidazole (Meim), and filling up to 10 mL with water. This resulted in a 0.01 M aqueous solution of Cu(Meim)_x(NO₃)₂. 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 in 5 mL of toluene, adding 20 µL (0.1 mmol) of sodium methoxide (30% solution in methanol), and filling up to 10 mL with toluene, which resulted in a 0.3 M solution of DMP and a 0.01 M solution of NaOMe in toluene.

In a typical quantitative, time-resolved dioxygen-uptake experiment (*vide infra*) performed using an in-house designed apparatus, 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. **Intense shaking**^[9] in a dioxygen atmosphere combined these solutions and started the reaction. The resulting reaction mixture was 3.33 mM in copper and 0.2 M in DMP. All polymerization reactions were performed at 25 °C under pure dioxygen under an atmospheric pressure. These are the conditions referred to as standard conditions. In this particular case, a Meim/Cu ratio of 30 and a NaOMe/Cu ratio of 2 were used. The catalytic activity were determined from the initial dioxygen-uptake rate R₀. At the end of the polymerization, the emulsion was broken by adding water or toluene to the reaction mixture. Thus, the copper catalyst could be easily removed by a simple extraction. The reaction selectivity for PPE was determined by diluting 1 mL of the reaction mixture with toluene and measuring the UV absorbance of DPQ at 421 nm. The polymer was isolated by precipitation from methanol. A detailed description of the dioxygen-uptake experiments and the processing of the experimental data were previously published.^[10]

Acknowledgements

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