Poly(9,9′-spirobifluorene-manganese porphyrin): a new catalytic material for oxidation of alkenes by iodobenzene diacetate and iodosylbenzene†

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Anodic oxidation of tetraspirobifluorene-manganese porphyrin lead to the coating of the working electrode by insoluble electroactive poly(9,9′-spirobifluorene-manganese porphyrin) films for which electrochemical behaviour and physicochemical properties are described; these polymeric materials are able to catalyze the heterogeneous epoxidation of styrene with iodobenzene diacetate and iodosylbenzene.

Metalloporphyrins have found uses as oxidation catalysts often showing high regio- and enantioselectivity.[1] Thus they are good candidates for immobilization on solid supports since they would be more cost-effective as recoverable and recyclable catalysts.[2–4] Electropolymers as supports for recoverable catalysts offer another elegant strategy which is much less developed.[5–9] Due to the orthogonal disposition of its fluorene groups and to the lack (or weak) direct conjugation of the π-electronic systems, 9,9′-spirobifluorene-manganese porphyrin[10,11] is a promising candidate to polymerize along two perpendicular dimensions leading to a material showing the beneficial properties of a polymer bearing well-isolated metalloporphyrin sites. Actually, the spirobifluorene segment which consists of two mutually perpendicular π-systems connected via a common insulating tetracoordinate atom, reduces the probability of interchain interactions and prevents the close packing of the polymer chains, resulting in good stability of polymers, as previously reported.[12] Spiro derivatives also provide a potentially useful stereochemistry that makes the molecules suitable for interconnection in future molecular devices.[13] Three dimensional polymers can be prepared by anodic oxidation of spirobifluorenes.[14] In this context, we describe here the electrochemical polymerization of a novel series of tetraspirobifluoreneporphyrins complexed by manganese atom. In addition, the characterization of the resulting polyspirobifluorene-manganese porphyrin films (Figure 1) called **poly (1)** and their potential applications as heterogeneous oxidation catalysts of olefins are reported.†

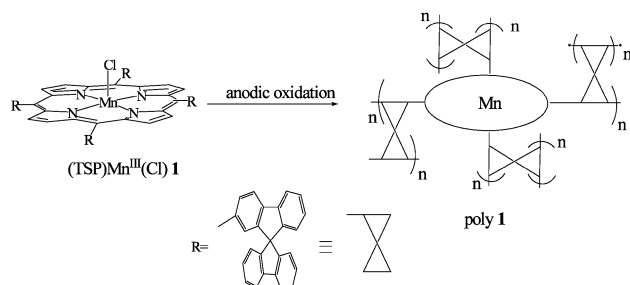Figure 2A presents the cyclic voltammograms (CVs) recorded during the anodic oxidation of **1** (1.3 10⁻³ M) and

Bu₄NPF₆ (0.2 M) in dichloromethane using a Pt working electrode. The CV recorded during the first anodic sweep exhibits the expected well-known two one-electron Mn porphyrin oxidation[15] at 0.66 and 1.18 V (ref Fc/Fc·⁺) respectively (Figure 2B). These two waves are followed by the irreversible spirobifluorene oxidation wave which has its at maximum 1.33 V. When scanning in a potential range including the three waves, the CVs show the appearance and the regular growth of a new reversible wave centered at 0.85 V and the continuous increase in amplitude of the other peaks. This indicates that a film is formed on the electrode as a consequence of electropolymerization through the spirobifluorene groups. Indeed, the electrode taken out of the electrochemical cell after the tenth sweep, rinsed in dichloromethane and studied in a new electrolytic solution free of any electroactive species presents the CV shown in Figure 2C. This CV presents two reversible waves with maxima at 0.9 and 1.2 V, corresponding to the oxidation of the metalloporphyrin unit and p-doping process of the polyspirobifluorene polymer.

Analysis of the material using scanning electron microscopy and electronic microanalysis gives a ratio C/Mn of about 117/1 in agreement with a conserved structure of monomers in **poly (1)** (Figure 1). The thickness of the deposits was measured between 50 and 100 μm. Figure 3 shows the UV-visible spectra of **1** and neutral **poly (1)**. The electronic spectrum of **1** in solution in CH₂Cl₂ (Figure 3A) presents several absorption
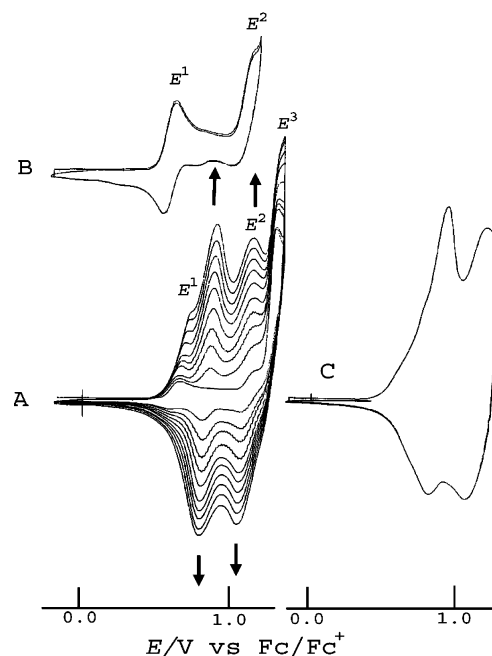

Fig. 1 Electrosynthesis of polyspirobifluorene-manganese porphyrin films.

Fig. 2 Cyclic voltammetry in CH₂Cl₂ (Bu₄NPF₆, 0.2M) sweep rate: 100 mV s⁻¹. A: (TSP)MnCl (1.3.10⁻³ M), 10 recurrent cycles; B: (TSP)MnCl (1.3.10⁻³ M), 1 sweep between 0.0 and 1.23 V; C: Poly(TSP)Mn(Cl), working electrode: Pt disk modified in A during oxidation of complex **1**.

bands at 381, 407, 525, 578 and 615 nm and a main absorption band at 480 nm. The electronic spectrum of neutral **poly (1)** obtained as a thin film on a platinum surface by anodic oxidation of a solution of **1** at 1.55 V and then undoped at 0.0V is presented in Figure 3C. Two main bands are observed at 480 and 615 nm, with an additional absorption band which maximum is at 360 nm and fits with the main aborption of the poly(spirobifluorene) (Fig. 3B). This relatively large band hides the bands observed at 381 and 407 nm in monomer **1**. After preparative electrosyntheses, the working electrodes were rinsed with solvents and the solid film polymers removed from the anode and dried under vacuum. The oxidatively formed films of the metalloporphyrins are insoluble in a variety of common solvents, such as acetone, dichloromethane, methanol, acetonitrile and dimethyl sulfoxide.

Following, the successful synthesis of the Mn porphyrin polymers, their catalytic activity was initially tested in the epoxidation of styrene. After scratching the film out of the electrode, the polymer was crushed to obtain a fine powder. The catalytic essay involved the use of iodobenzene diacetate (Table 1, conditions A) and iodosylbenzene (Table 1, conditions B) as possible oxidants and imidazole as the axial ligand for the metalloporphyrin. The activity of the polymer catalyst was first tested with iodobenzene diacetate which has not been frequently used in metalloporphyrin-catalyzed oxidation reactions[16] and
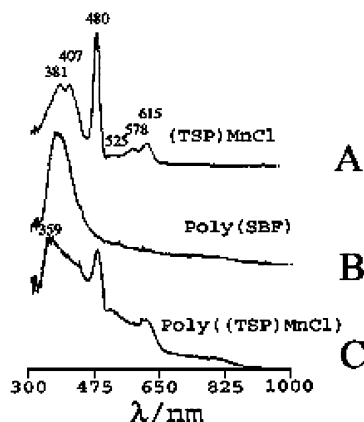

Fig. 3 UV-Vis spectra of (TSP)Mn **1**,poly(SBF), poly(TSP)Mn (**poly (1)**)

Table 1 Epoxidation of alkenes by **1** and **poly (1)** using iodosylbenzene or iodobenzene diacetate as oxidant.

Catalyst	Oxidant	Alkene	Yield (%)[a]	Epoxide aldehyde
Poly (1)	PhI(OAc)$_2$[b]	Styrene	65	2
		4-Chlorostyrene	60	3
	PhIO[c]	Styrene	70	1.7
		4-Chlorostyrene	50	3.8
1	PhI(OAc)$_2$[b]	Styrene	71	1.7
		4-Chlorostyrene	71	4
	PhIO[c]	Styrene	75	1.9
		4-Chlorostyrene	73	4

[a] Yield based on starting olefin at room temperature. [b] *Conditons A*: Time reaction: 90 min. (P)MnCl/iodobenzenediacetate/imidazole/alkene (1/100/10/1000) in dichloromethane/acetonitrile (2:1). [c] *Conditions B*: Time reaction: 90 min for **1** and 180 min for **poly (1)**. (P)MnCl/ iodosylbenzene/imidazole/alkene(1/100/10/1000)in dichloromethane.

the results compared to the corresponding soluble monomer **1**. The styrene epoxidation reaction was monitored by gas chromatography and styrene oxide was found to be the major product in all cases (Table 1). Thus it should be noted that **poly (1)** catalysts have efficiencies similar (or very close) to those of the corresponding metalloporphyrin complexes in solution, even with PhIO, which is almost insoluble in dichloromethane. Thus this reaction, which is actually a triphasic system solid/ solid/liquid (polymeric PhIO/**poly (1)**/styrene) yielded 70% epoxide after 3 h.

To test a possible regioselectivity of the polymer *vs* monomer, competitive catalytic oxidation was performed with a 1:1 mixture of styrene and cyclooctene. With complex **1**, the styrene oxide/cyclooctene oxide ratio was about unity whereas we detected a twofold excess of styrene oxide with the **poly (1)**. In these external competition experiments, a 10:1 alkene to oxidant ratio was used in order to avoid the formation of over-oxidized products. Plausible explanation for this moderate regioselectivity is the presence of crowded environment in the polymer which would restrict the approach of the internal olefin.

The recovery and recyclability of the manganese spirobi-fluorene polymers have been also examined. The catalysts were first tested for activity in the epoxidation of styrene with iodobenzene diacetate leading to 8 recycling steps without decrease of activity (yield for each turn between 58 and 68%, catalyst: 3 mg). Furthermore the resistance of the catalyst towards oxidative degradation was also tested in the epoxida-tion of styrene in stoichiometric experiment (oxidant/olefin ratio = 1); progressive addition of iodobenzene diacetate to olefin leads to 60% conversion. This reaction can be re-produced: after several washes, the manganese polymer was still efficient in olefin epoxidation without any loading of metalloporphyrins in solution.

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