

Poly(ruthenium carbonyl spirobifluorenylporphyrin): a new polymer used as a catalytic device for carbene transfer†

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Received (in Cambridge, UK) 30th May 2003, Accepted 1st August 2003

First published as an Advance Article on the web 19th August 2003

Oxidative electropolymerization of tetraspirobifluorenyl porphyrin ruthenium(II) carbonyl complexes can be used to coat Pt electrodes with polymeric films; after being removed from the electrode, these polymeric materials are able to catalyze the heterogeneous cyclopropanations and 2,3 sigmatropic rearrangements with ethyl diazoacetate.

Solid-state reactions constitute an important area of selective organic reactions.¹ Thus there are many examples of electropolymers, in which the deposit is directly used as a catalyst, taking advantage of the electrode.^{2,3} To the best of our knowledge, however, electropolymers have seldom been used as catalysts after being removed from the electrodes. In fact, electropolymerized metalloporphyrin films have so far been mainly used as a catalytic electrode material for olefin epoxidation, biosensors and solar energy conversion.² We are particularly interested in the preparation of metalloporphyrin network materials as a new generation of catalysts. In an ideal case, the supported complexes can be recovered from reaction mixtures by simple filtration, they can be recycled and they can help selectivity. Metalloporphyrin molecules show a remarkable diversity not only in oxidation^{4,5} but also in carbene transfer catalysis.^{6,7} We have recently shown that poly(tetraspirobifluorene porphyrin) complexed by manganese showed potential applications as heterogeneous catalysts for oxidation of olefins with iodobenzene diacetate and iodosylbenzene.⁸ The present work will focus on carbene transfer to olefins and sulfides using ruthenium spirobifluorenylporphyrin polymers (Fig. 1). The ruthenium porphyrin monomers are prepared by treatment of tetraspirobifluorene porphyrin with Ru₃(CO)₁₂ in *o*-dichlorobenzene at 160 °C (2 h) as previously reported.⁹ After preparative macroelectrosyntheses at fixed potential (1.4 V), the working electrodes were rinsed with

solvents and the solid film polymer was removed from the anode, dried under vacuum and scratched in order to obtain a fine totally insoluble powder.

Fig. 2A–B presents the cyclic voltammograms (CVs) recorded during the anodic oxidation of **1** (2.2×10^{-3} M) in CH₂Cl₂ + Bu₄NPF₆ (0.2 M) using a Pt working electrode. The CV recorded during the first anodic sweep exhibits the expected well-known two reversible one-electron Ru porphyrin oxidation waves at 0.46 and 0.89 V (ref. Fc/Fc⁺), respectively (Fig. 2A).^{10,11} These two waves are followed by the irreversible spirobifluorene oxidation wave with a maximum at 1.37 V. When scanning in a potential range including the three waves, the CVs show the appearance and the regular growth of two new reversible waves centered at 0.65 and 1.08 V and the continuous increase in amplitude of the other peaks (Fig. 2B). 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 then studied in a new electrolytic solution free of any electroactive species, presents the CV shown in Fig. 2C. This CV shows four reversible waves with maxima at 0.42, 0.68, 0.81 and 1.08 V, corresponding to the oxidation of the metalloporphyrin unit (0.42 and 0.81 V) and the p-doping process of the spirobifluorene polymer (0.68 and 1.08 V).

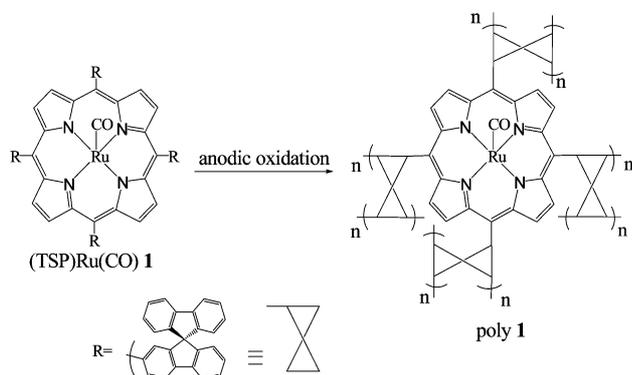


Fig. 1 Electropolymerization of **1**.

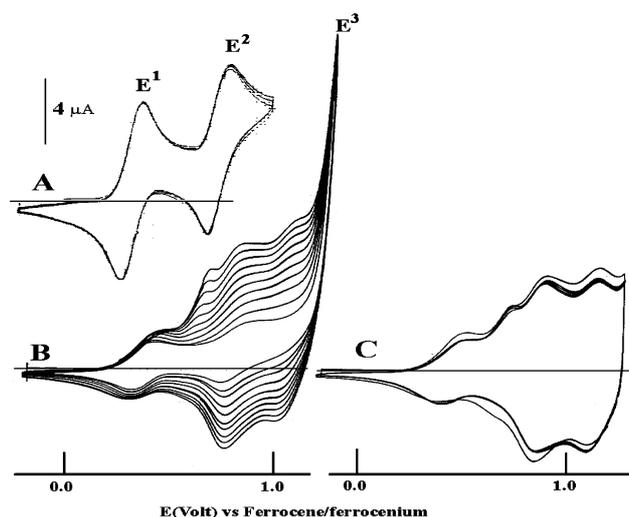


Fig. 2 Cyclic voltammograms (CVs) recorded during the anodic oxidation of a 2.2×10^{-3} M solution of (TSP)RuCO in CH₂Cl₂ + 0.2 M Bu₄NPF₆ using a Pt working electrode. 2A: first anodic sweep of (TSP)Ru(CO) between 0 and 1 V. 2B: Ten anodic sweeps of (TSP)Ru(CO) between 0 and 1.4 V. 2C: Three anodic sweeps of poly(**1**) film formed on the electrode between 0 and 1.2 V.

† Electronic supplementary information (ESI) available: experimental details. See <http://www.rsc.org/suppdata/cc/b3/b306021g/>

In order to study the behaviour of poly(**1**), spectroelectrochemical experiments were performed. UV-vis spectral changes monitored during anodic oxidation of poly(**1**) in $\text{CH}_2\text{Cl}_2 + \text{Bu}_4\text{NPF}_6$ (0.2 M) are shown in Fig. 3. The electronic spectrum of neutral poly(**1**) obtained as a thin film on an ITO glass electrode showed two main bands at 350 and 426 nm, due to the neutral spirobifluorene chains and ruthenium porphyrins, respectively (Fig. 3, 0 V). We can also observe bands at 534 and 576 nm (Q bands) similar to those of the monomer (533 and 569 nm). After progressive oxidation to 0.54 V, all bands decrease in intensity as a new well-defined band starts to grow in at 650 nm. These data suggest the formation of a transient species, the ruthenium carbon monoxide porphyrin radical cation.¹¹ This band disappears rapidly which indicates a transformation of the radical inside the polymer. The final oxidation product (1.24 V) has a UV-vis spectrum with a broad peak at 524 nm and a relatively low molar absorptivity compared to the neutral polymer, which is characteristic of a polyspirobifluorene in its *p*-doped state.¹² As expected, the IR spectrum of poly(**1**) showed a CO vibration at 1949 cm^{-1} in KBr very close to the value observed in the monomer (1939 cm^{-1}).¹¹ Analysis of the material using scanning electron microscopy and electronic microanalysis gives a ratio C : Ru of about 120 : 1 in agreement with a conserved structure of monomers in poly(**1**).

Following the successful synthesis of the Ru porphyrin polymers, their catalytic activity was initially tested in carbene transfer catalysis. The catalytic studies involved the use of diazoethyl acetate as a possible carbene precursor with styrene or methyl allyl sulfide as substrates. The activity of the polymer catalyst was first focused on methyl allyl sulfide which has not been frequently used in metalloporphyrin-catalyzed carbene transfer reactions¹³ and the results were compared to those for the corresponding soluble monomer **1**. The reaction was monitored by gas chromatography and carbene insertion was found to be the major reaction in all cases. Treatment of methyl allyl sulfide with ethyl diazoacetate at 25 °C in the presence of the ruthenium polymer results in the formation of ethyl 2-(methylthio)pent-4-enoate with 87% yield (Fig. 4). The formation of this compound derives from the [2,3]-sigmatropic

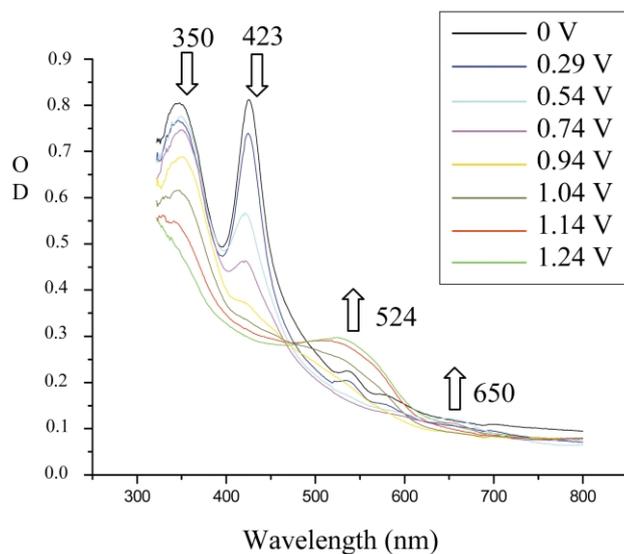


Fig. 3 Spectroelectrochemical experiments on poly(**1**) recorded from 0 V to 1.7 V (reference Fc/Fc^+).

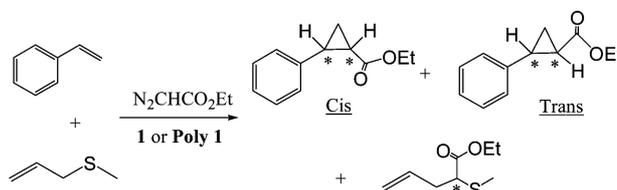


Fig. 4 Competitive reactions of carbene transfer (cyclopropanation/sigmatropic rearrangement) with **1** or poly(**1**).

rearrangement of the sulfur ylide.¹⁴ Poly(**1**) also^{15,16} catalysed decomposition of ethyl diazoacetate in the presence of styrene resulting in the formation of the corresponding cyclopropane in 85% yield with a large excess of the *trans* isomer (*trans* : *cis* ratio: 9 : 1). Similar results were obtained with the monomer (see supplementary material† for details). The recovery and recyclability of poly(**1**) have also been examined, leading to 7 recycling steps without decrease of activity.

To test a possible regioselectivity of the polymer vs. monomer, competitive catalytic carbene transfer was performed with a 1 : 1 mixture of styrene and allyl methyl sulfide. With complex **1**, the sigmatropic : cyclopropanation reaction ratio was about 65 : 35 whereas we detected an increase of the sigmatropic rearrangement with the poly(**1**) (78 : 22). In these external competition experiments, a 10 : 1 substrate to diazo ratio was used in order to avoid the formation of over-addition products. A plausible explanation for this different regioselectivity is the presence of a crowded environment in the polymer which would restrict the approach of the aromatic olefin. Electropolymerization of metalloporphyrins bearing only one spirobifluorene group will open a new route to less crowded active sites. Future studies will focus on developing stereoselective versions of these reactions using chiral ruthenium polymers.

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