Electronic Supplementary Information

Synthesis of $[Rh_2(form)_2(MA\text{-}COO)_2]$ (**1**).

Reactions with CO

Instruments

Figure 1 ESI. a) Positive MALDI-TOF mass spectrum of $[Rh_2(form)_2(MA\text{-}COO)_2]$: b) the peak of $[Rh_2(form)_2(MA\text{-}COO)_2]^{H+}$, experimental (continuous line) and of its simulated (dashed line, resolution about 1800 [FWHM]) isotopic distribution species

Figure 2 ESI. UV-visible spectra of copolymers **2-4** and PMMA

Figure 3 ESI. GPC traces of copolymer **2**

Figure 4 ESI. Positive MALDI-TOF mass spectrum of copolymer **3**.

Synthesis of $[Rh_2(form)_2(MA\text{-}COO)_2]$ (1).

An acetone solution (5 mL) of $[Rh_2(form)_2(CH_3CN)_6][BF_4]_2$ (0.200 g, 0.186 mmol) or $[Rh_2(form)_2(CF_3COO)_2(H_2O)_2]$ (0.170 g, 0.186 mmol) was added to a stirred water solution (20 mL) of potassium 2-(methacroyloxy)ethylphthalate (0.588 g, 1.86 mmol) and the resulting mixture left to stir for ca. 10 min. The resulting green solid was collected by filtration and dried at 50 °C (24 h). The crude solid was then dissolved in diethyl ether (30 mL) and the resulting solution filtered. By removal of the solvent under reduced pressure **1** was obtained as a green solid. Yield 85 %.

Reactions with CO

Carbon monoxide was bubbled through a $CHCl_3$ solution of **1**. Immediately the solution color changes from green to red violet indicative of the CO-[Rh_2(form)$_2$(MA-COO)$_2$] adduct formation, as confirmed by the appearance in the IR spectrum of a ν(CO) band at 2062 cm^{-1} while in the UV-vis an absorption at 552 nm appears. The reaction is reversible and the solution left in air, in 1 hour releases CO restoring **1,** quantitatively.

The same reaction occurs in a solid state. When a solid sample of **1** was flowed, at atmospheric pressure and room temperature, with carbon monoxide for 2 min, readily the starting green color turned dark-red, while in the IR spectrum an intense CO absorbtion was formed at 2062 cm^{-1}, consistent with the formation of the related CO adduct. In agreement with IR data, CO releasing occurs in ca. 60 h at r.t. and in 24 h at 40 °C.

While the reactions in $CHCl_3$ of **2-4** with CO proceeds as observed for **1**, solid samples of copolymers **2-4** flowed with carbon monoxide did not give any spectroscopically evidence of CO absorption.

Instruments

Apparatus. IR spectra were recorded on KBr pellets with a Perkin-Elmer RX I FT-IR spectrometer. NMR measurements were performed with a Bruker AMX 300 spectrometer using standard pulse sequences. UV-visible spectra were recorded on a Shimadzu Model 1601 spectrophotometer. Electrochemical measurements were carried out in argon-purged 1,2-dichloroethane at room temperature with a PAR 273 multipurpose equipment interfaced to a PC. The working electrode was a glassy carbon (8 mm^2, Amel) electrode. The counter electrode was a Pt wire, and the quasi-reference electrode was an Ag wire (ferrocene was used as internal standard). The concentration of the complex was about 5×10^{-4} M. Tetrabutylammonium hexafluorophosphate was used as supporting electrolyte and its concentration was 0.05 M.

A PL-GPC 110 (Polymer Laboratories) thermostated system, equipped with three PL-gel 5µm columns (two Mixed-D and one Mixed-E) attached in series, was used. The analyses were performed at 35±0.1 °C using THF as eluant at a flow rate of 1 mL/min. A differential refractometer (Polymer Laboratories) and an UV–Visible spectrophotometer (Hewlett Packard series 1050, fixed at 334 nm), connected in parallel were used as detectors. The instrument was calibrated with five poly(methylmethacrylate) standards using PL-Caliber GPC software for the determination of average molecular masses and Polydispersity of the polymer samples. MALDI-TOF mass spectra were acquired on a Voyager DE-STR (PerSeptive Biosystem) with delayed extraction (20 kV applied after 233 ns, with a potential gradient of 2545 V/mm) and detection in reflection mode. The instrument was equipped with a nitrogen laser (emission at 337 nm for 3 ns) and a flash AD converter (time base 2 ns). Each MALDI experiment was performed by loading about 0.1 mmol of sample and 40 mmol of trans-3-indoleacrylic acid (IAA, used as a matrix) on the sampler target, using THF as a solvent. The mass calibration was performed as reported in previous cases.[1] Because of the isotopic composition, molecular species are detected in the mass spectra as clusters of peaks. To simplify their assignments, m/z values reported in the spectra and in the text are referred to the first peak of each cluster, corresponding to the ion containing the most abundant isotope of each element present. Differential Scanning Calorimetry (DSC) was performed to determine glass transition temperatures by using a Mettler DSC-20 instrument with a heating rate of 10 °C/min in N_2 atmosphere (40 mL/min).

[1] E. Scamporrino, D. Vitalini, P. Mineo, *Macromolecules*, **1996**, *29*, 5520.

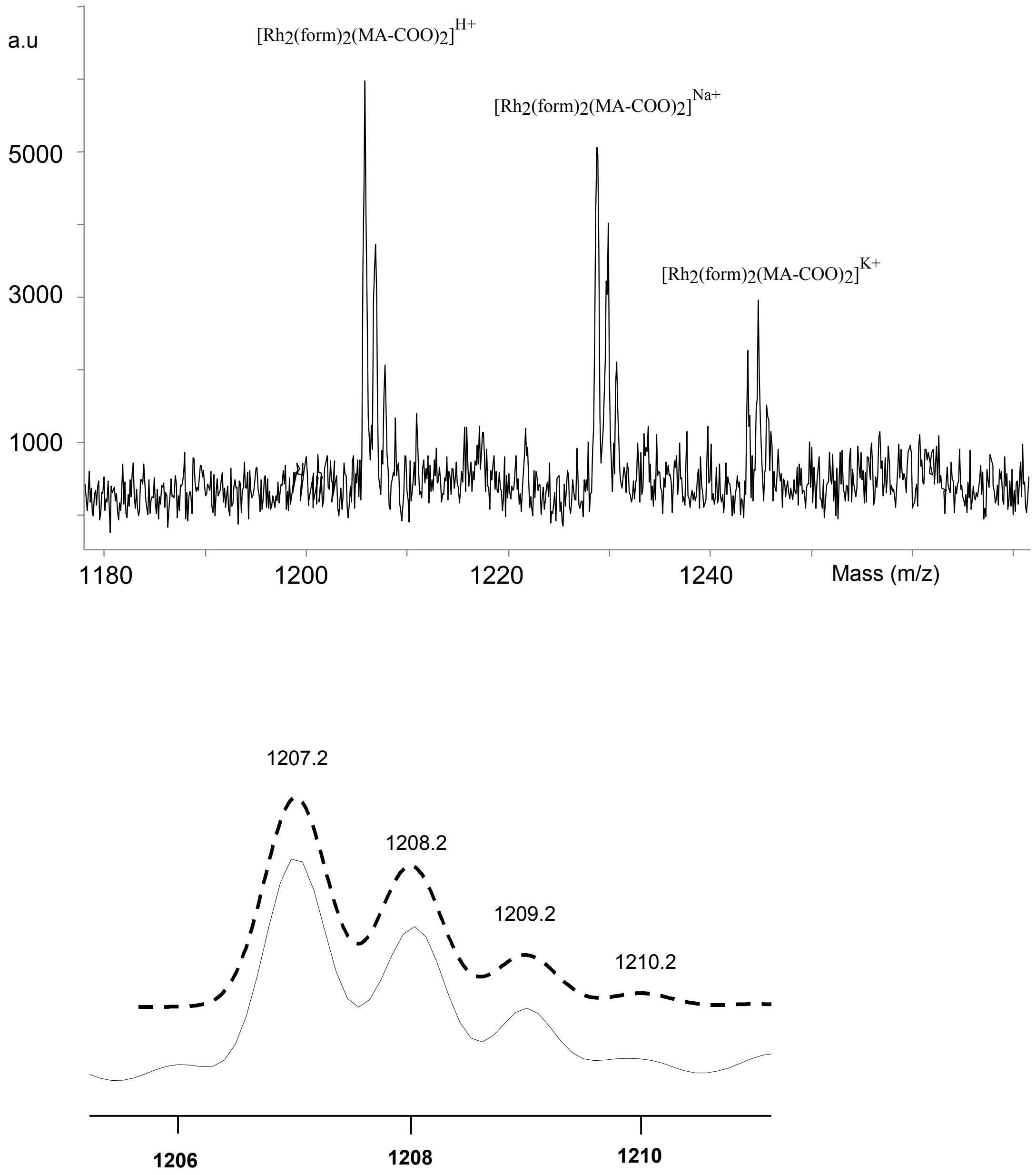


Figure 1. a) Positive MALDI-TOF mass spectrum of $[Rh_2(form)_2(MA\text{-}COO)_2]$; **b)** the peak of $[Rh_2(form)_2(MA\text{-}COO)_2]^{H+}$, experimental (continuous line) and of its simulated (dashed line, resolution about 1800 [FWHM]) isotopic distribution species.

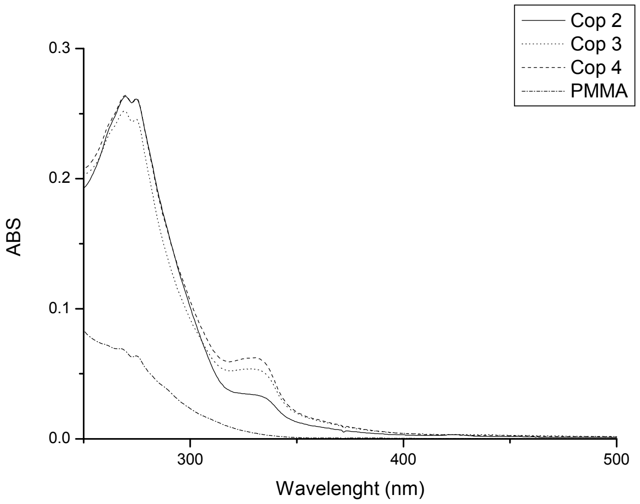


Fig. 2. UV-visible spectra of copolymers **2-4** and PMMA

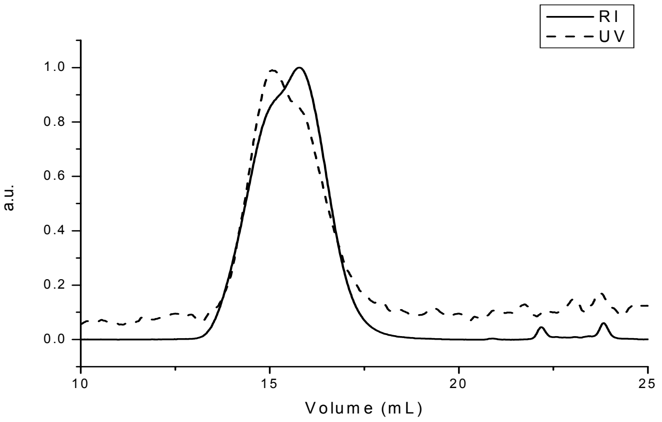


Fig. 3. GPC traces of copolymer **2**.

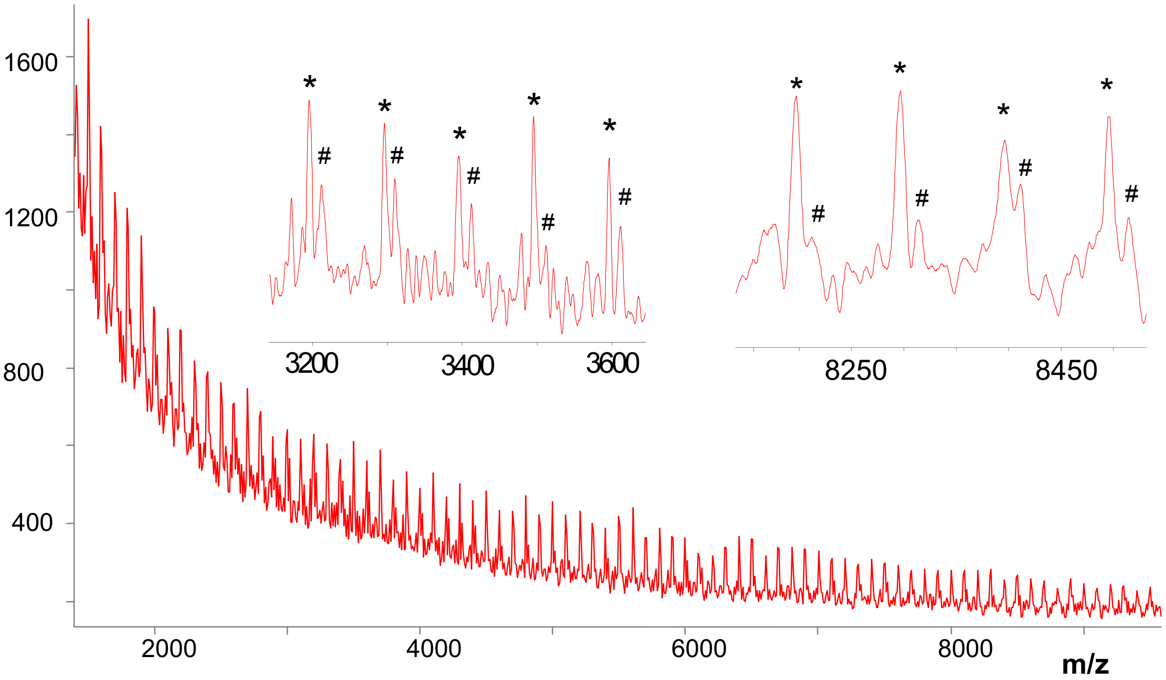
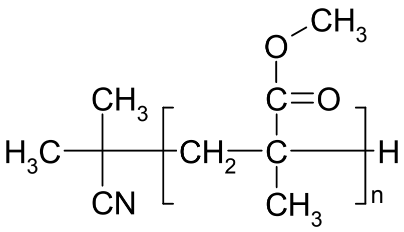


Fig. 4 ESI. Positive MALDI-TOF mass spectrum of copolymer **3.**

The positive MALDI-TOF spectrum of copolymer **3** is reported in Figure **1 ESI**. The spectrum essentially consists of a series of peaks at m/z 92 +n100 with n=10 (m/z 1094)÷120 (m/z 12094) and m/z 108 +n100 with n=10 (m/z 1110) ÷120 (m/z 12110), corresponding to molecular ions of polymer containing only MMA units with isobutyronitrile as end-group (see structure 1), detected as M_nNa^+ (*) and M_nK^+ (#), respectively.



$H_3C-C(CH_3)(CN)-[CH_2-C(CH_3)(COOCH_3)]_n-H$

structure 1