

Supplementary information

Bulky phosphite modified rhodium catalyst for efficient hydroformylation of disubstituted alkenes and macromonomers in supercritical carbon dioxide

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¹⁰ The reactor does not allow for any visual observation of the reaction mixture. During the hydroformylation experiments with **1**, **3**, **5**, **7**, and **9a** the samples were taken from the lower part of the reactor. The sum of the concentrations of the substrate(s) and reaction products found by GC analysis of the sample volume was on average 18% higher than expected when assuming that the substrate(s) and products were homogeneously distributed in the reactor volume.¹ The sample
¹⁵ volume is merely 0.17% of the total reactor volume. Therefore, it was not expected that extracting a relatively higher amount of substrate and products than CO₂ from the reactor would significantly affect the hydroformylation. This systematic deviation was likely caused by the difference in temperature of the reactor (90 °C) and the sample volume (estimated to be 30-40 °C) and was also observed in previous studies.² As a result of this temperature difference the fluid density in the
²⁰ sample volume was higher than in the reactor which resulted in higher concentrations of substrate(s) and reaction products in the sample volume than in the reactor. This was as expected; this phenomenon has been discussed in earlier related work with reactor set up used in this study.^{3,4}

Figure S1 shows the pressure-time histories corresponding to the experiments collected in
²⁵ Table 1 of the manuscript. Figure 1 shows that the differences in conversion rate of substrates **1** to **9** (Table 1) are reflected in pressure-time histories of the respective substrates. Before addition of the alkene substrate the pressure is about 34 MPa (t ≈ 0 h). Possible differences in the interaction

of the alkene with the CO₂/CO/H₂/catalyst mixture can be inferred from the maximum pressure reached just after injection of the alkene. For **9a** the highest pressure reached equals 38 MPa. For the other substrates the maximum pressure reached was about 36 MPa. Generally, the pressure at maximum conversion was above 26 MPa. Therefore, overall the differences in interaction of the aldehydes with CO₂ appear to be small under these conditions. Comparing our conditions with literature data on phase equilibria, for the binary system CO₂-**3**, single phase conditions were found above approximately 14 MPa at 80 °C, independent of the composition.⁵ For the binary system CO₂-**5**, single phase conditions were found above approximately 14 MPa at 105.5 °C independent of the composition.⁶ Considering that the lowest pressure reached at a high substrate conversion was about 26.6 MPa at 90 °C during the hydroformylation of **7**. Taking into account the above considerations it is very likely that the reaction mixtures with respect to reactants, products and solvent, were single phase at the start of the reaction.

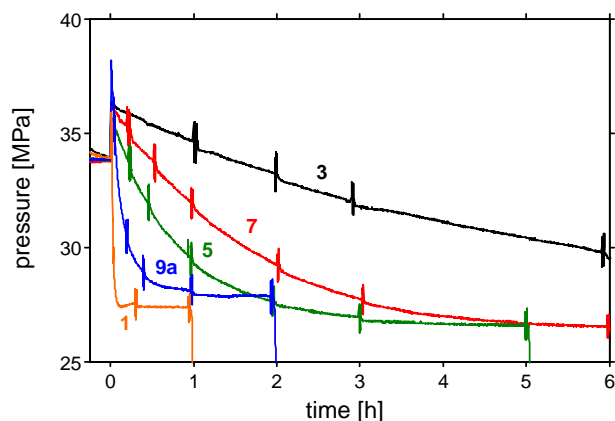


Fig S1. Pressure – time histories for the experiments described in Table 1.

Further indirect proof of the occurrence of single phase reaction mixture during the hydroformylation of the monomers was derived by considering the sum of the concentration of the liquid reactants and products (alkenes and aldehydes) found in the sample volume. Note that the sample volume was not heated to reactor temperature (Figure S2).

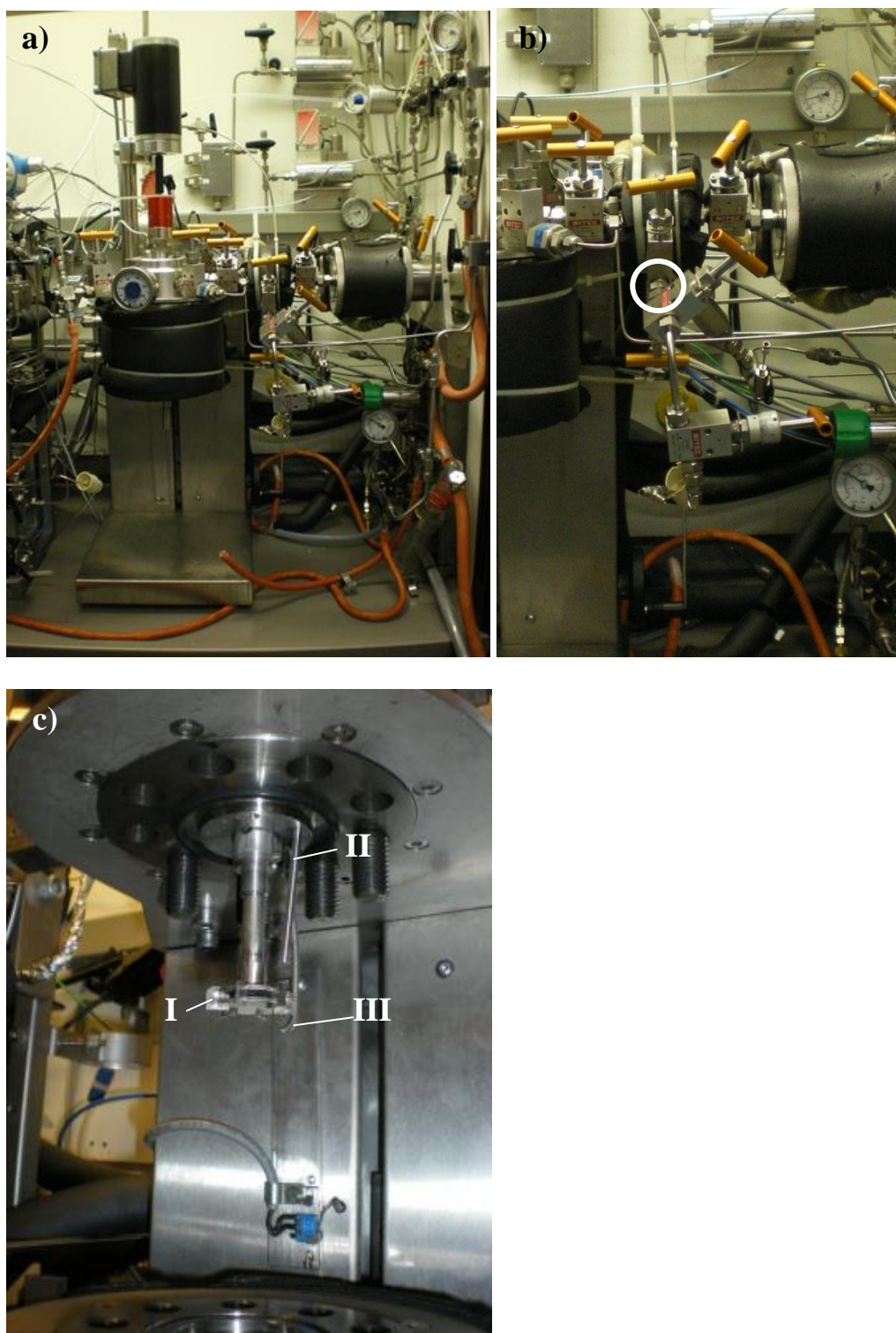


Fig. S2. Pictures of the high pressure reactor used in this study. a) overview of reactor and infrastructure; b) sampling section, area within the white ellipse indicates the sample volume; c) overview of internals of the reactor with I as the magnetically coupled stirrer, II as the thermowell that contains the Pt100 temperature sensor, and III as the tubing enabling sampling from the bottom of the reactor.

An advantage of this is that the reaction will proceed at a much slower rate in the sample volume
and upon expansion (depressurization) the sample will cool rapidly decreasing the reaction rate

even further. However, a disadvantage is that the density of the sample will be higher than the density in the reactor. In this study 90 °C is used as the reaction temperature. As an approximate temperature of the sample volume 55 °C can be taken, which is the mean of the reactor temperature and room temperature. To illustrate the effect of temperature one can compare the density of pure carbon dioxide as a function of pressure at 55 and 90 °C (Figure S2).⁷ As an estimate of the ratio in density of the reaction mixture at 90 and 55 °C the ratio in density of pure carbon dioxide at 90 and 55 °C was taken. The sum concentration of reactants (excluding H₂ and CO) and products was corrected for the difference in temperature between reactor and sample volume. The observed total concentration and the total concentration corrected for the temperature difference are plotted in Figure S3. It is clear that when the concentration are corrected for the temperature difference between reactor and surroundings, the values of concentration will be closer to the expected total concentration which can be calculated from the amount of alkene substrate injected (typically 0.05 mol) and the reactor volume (0.108 L). This is indirect proof that the reactions were carried out under single phase conditions with respect to reactants and products.

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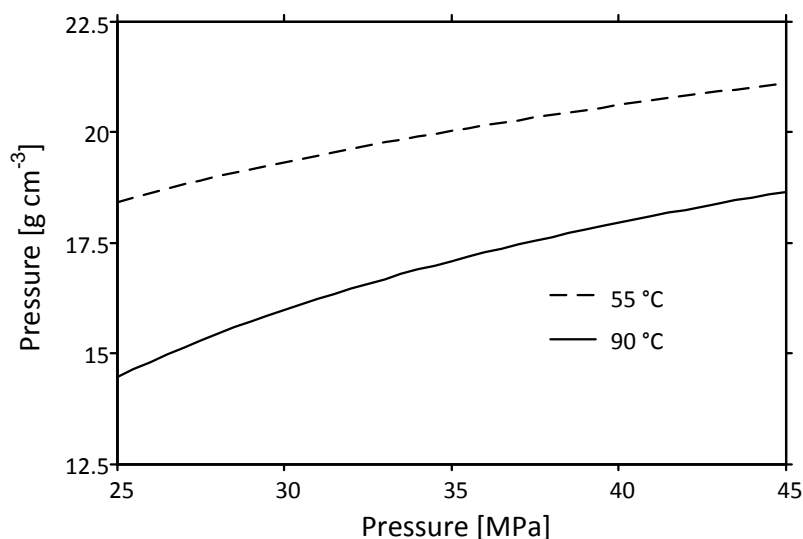


Fig S2. Density of pure carbon dioxide as a function of pressure at 55 and 90 °C.

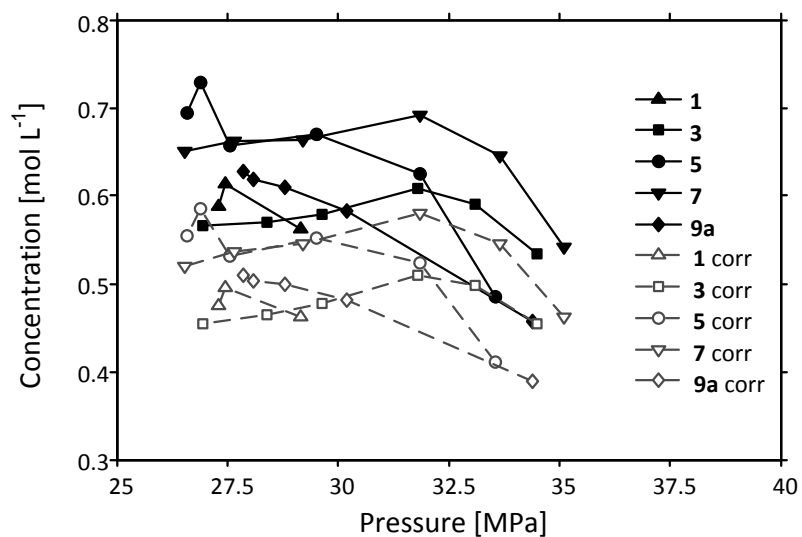


Fig S3. Observed total concentration (sum of liquid reactants and products) for the hydroformylation of **1**, **3**, **5**, **7**, and **9a** at _s depicted with the closed black markers. The total concentrations corrected for the temperature difference between reactor and sample volume are depicted with open markers.

In Figures S4 and S5 pictures of the reactor containing macromonomer **11** (polystyrene) and **13** (polymethylmethacrylate), respectively are given.

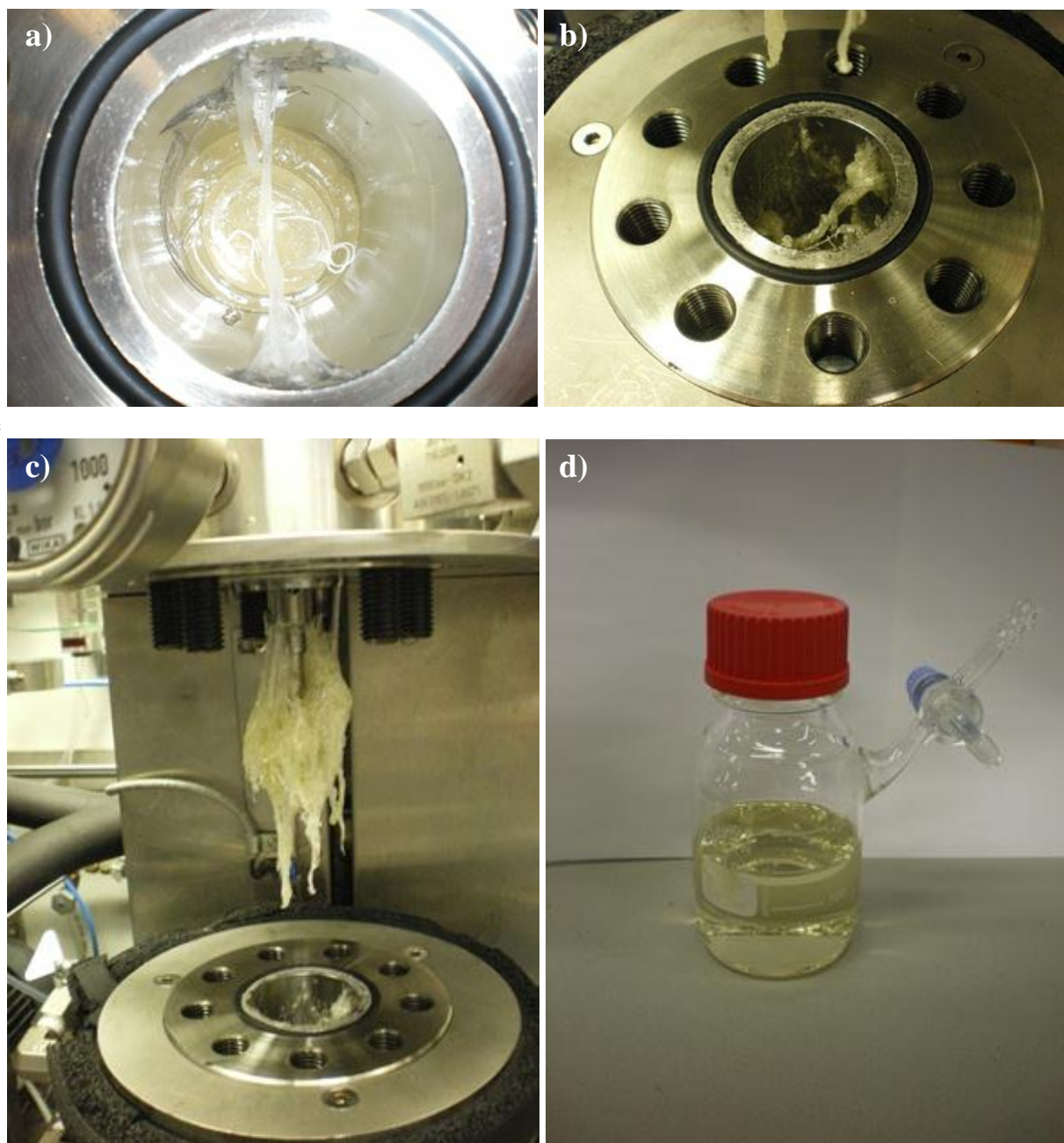


Fig. S4. Pictures of the macromonomer **11** before and after hydroformylation. a) fresh macromonomer loaded in the bottom part of the reactor; b) hydroformylated macromonomer in the bottom part of the reactor; c) hydroformylated macromonomer sticking to the internals of the reactor; d) 250 mL flask containing 125 mL tetrahydrofuran and 84% of the hydroformylated macromonomer.

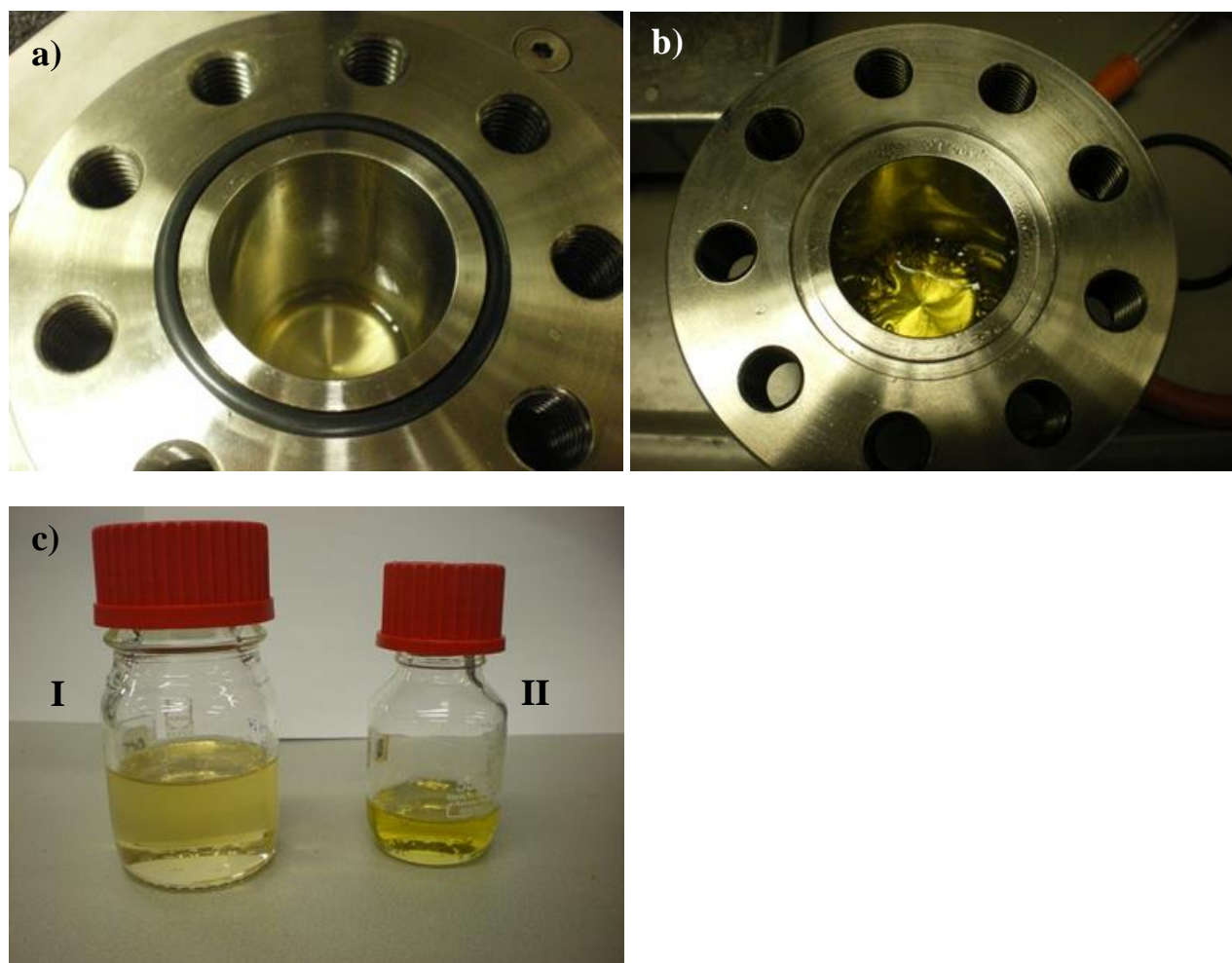


Fig. S5. Pictures of the macromonomer **13** before and after hydroformylation. a) fresh macromonomer loaded in the bottom part of the reactor; b) hydroformylated macromonomer in the bottom part of the reactor; c) On the left (I) 100 mL flask containing 50 mL fresh macromonomer **13** and on the right (II) a 50 mL flask containing the hydroformylated macromonomer **13**.

10 References

- 1 The highest deviation of the concentration in the sample volume in comparison with the substrate concentration, assuming homogeneous distribution of the substrate in the reactor, was 35% and was observed during the hydroformylation of **7**.
- 2 A. C. J. Koeken, *J. Mol. Catal. A*, 2011, **346**, 1-11.
- 3 At a reaction temperature of 70 °C using 0.1 mol of **13b** as substrate and a higher density of CO₂ (0.63 g mL⁻¹) a maximum deviation of 12% was found, also when sampling was done from the top part of the reactor. See references 31 and 49 of the manuscript. In the case of pure carbon dioxide the density at 30 °C and 26 MPa is about 42% higher than the density at 90 °C and 26 MPa.
- 4 A. C. J. Koeken, M. C. A. van Vliet, L. J. P. van den Broeke, B.-J. Deelman, J. T. F. Keurentjes, *Adv. Synth. Catal.* 2006, **348**, 1553–1559.
- 5 A. Bamberger, J. Schmelzer, D. Walther, G. Maurer, *Fluid Phase Equilibria* 1994, **97**, 167- 189.
- 6 M. Lora, M. A. McHugh, *Fluid Phase Equilibria* 1999, **157**, 285–297.
- 7 Data on carbon dioxide density were obtained from <http://webbook.nist.gov/chemistry/> on 26th of November 2012.