

SUPPLEMENTARY INFORMATION

Solubility and activity of a phosphinosulfonate palladium catalyst in water with different surfactants.

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1. Experimental section

a. Materials.

All manipulations of metal complexes were carried out under an inert atmosphere using glove box or Schlenk techniques. Solvents were dried and degassed. Deionized water was degassed with argon before use. Surfactants solution in water were prepared in advance and were degassed before use. Unless otherwise stated reagents obtained from the commercial supplier were used without any purification. Ligand L₁ was obtained from Sigma Aldrich.

Rhodafac[®] RS-610 was obtained from Solvay and Tergitol[®] 15-S-20 was obtained from Dow.

b. Instrumentation.

Transmission electron microscopy images were obtained using JEOL 2100 Cryo microscope. High temperature NMR were acquired on the UI600 NMR a VARIAN UNITY INOVA 600 NB equipped with a 5mm Varian AutoTuneX ¹H/X PFG Z probe. Particles size distribution were measure by DLS on a Malvern Zetasizer ZS90. UV-vis was performed using a Varian Cary 50 Bio. DSC was performed on a Perkin Elmer Diamond DSC.

c. UV-vis measurements

- *Calibration*

The UV calibration was done by preparing a 1.5g/L stock solution of 1-Pd-NH₂PEG catalyst in water/Rhodafac[®] (8 g/L). This stock solution was further diluted with water/Rhodafac[®] solution and run on the UV-vis instrument using a closed 2mL cuvette.

- *Preparation of 1-Pd-DMSO UV sample*

In 20mL vial sealed with a septum cap, 10mL of water/Rhodafac[®] (8 g/L) was degassed and placed in an oil bath at 85°C. The vial was connected to a schlenk line. Catalyst solution, 0.1mL (20µmol/mL 1-Pd-DMSO or 1-Pd-pyr in DCM) was directly injected in the stirring water/surfactant solution. A needle is placed on the vial septum to allow the vaporized DCM to escape. After 5min

the needle is removed and the vial was taken out of the oil bath. 2mL of this solution was transfer into the UV cuvette for analysis.

d. Catalyst Synthesis

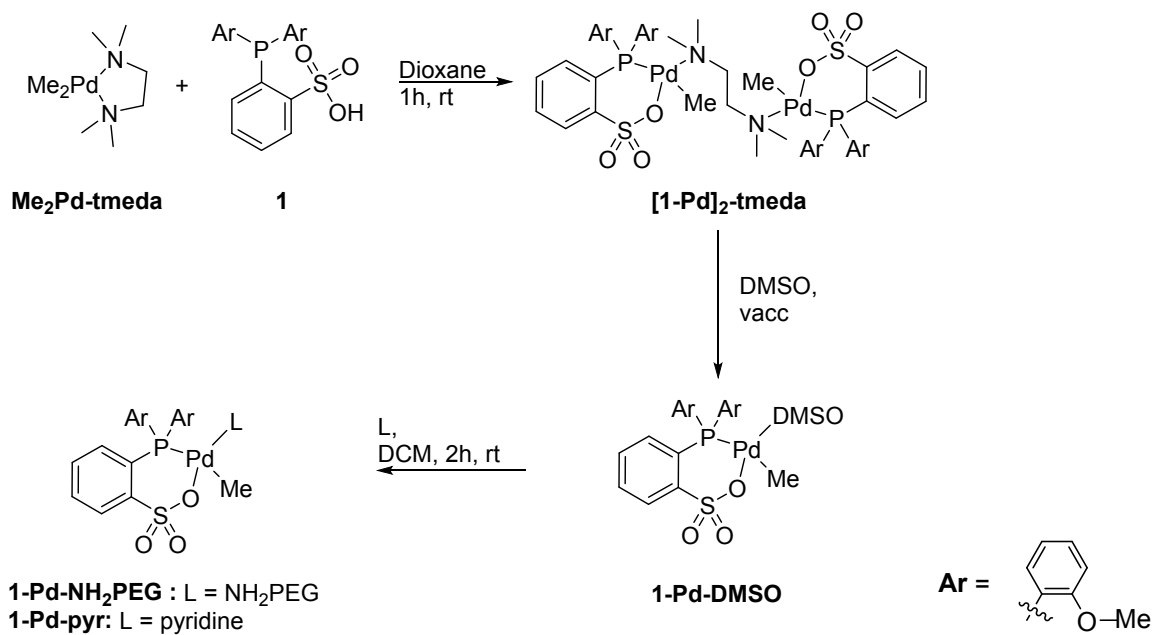


Figure S1 Catalyst synthesis pathway

Me₂Pd-tmeda, **1-Pd-DMSO**, **1-Pd-pyr** and **1-Pd-NH₂PEG** pre-catalysts were synthesized according to previous literature report.^{1,2}

e. Ethylene Polymerization

All ethylene polymerizations were carried out in a mechanically stirred (1000 rpm) a 100 mL stainless steel high-pressure reactor equipped with a heating and cooling jacket and thermocouple. The ethylene pressure was kept constant throughout the polymerizations. Before each polymerization run, the reactor was purged under vacuum at 85°C before to be backfilled with argon. Three cycles of vacuum-and-backfilling with argon were repeated before the transfer of reagents in the reactor.

- ***Polymerization in water***

100mL of surfactant/water solution were transfer into the pre-heated (85°C) ethylene polymerization reactor. The catalyst precursor solution in DCM (20 μ mol/mL) was added to the reactor. The reactor was pressurized to achieve the desired pressure in the vessel and polymerization was run for the desire polymerization time. The reactor was then vented and brought to room temperature.

The reaction solution was filter thru glass wool to remove PE coagulate.

Specific weights of reaction solution were dried at 120°C overnight.

TO were calculated via gravimetric analysis using the weight difference of dry samples before and after ethylene polymerization.

PE coagulate was collected and dried at 120°C overnight.

f. Detailed data from polymerizations of Fig. 4

Table S1. Polymerization of ethylene with 1-Pd-DMSO overtime^a

entry	Surfactant	Time [h]	TO	PS (nm)	% coag
S1	Rhodafac [®]	0.5	660	160	18
S2		1	1260	286	20
S3		1.5	1855	314	16
S4 ^c		6	4920	287	17
S5	SDS	0.5	164	54	-
S6		1.5	644	69	-

^aPolymerization was carried out with 20 μ mol of catalyst at 85 °C in 100mL of water with Rhodafac[®] RS-610 : 0.8g or SDS: 0.75g ^b g/mol. ^c 1.6g surfactant used

2. DLS data

The particle size distribution was recorded by intensity.

Table 1 entry 1

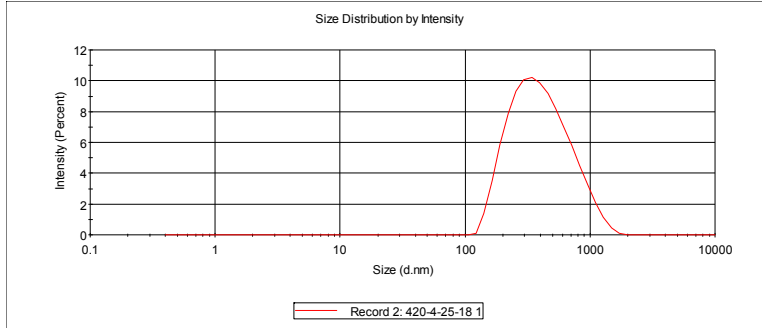


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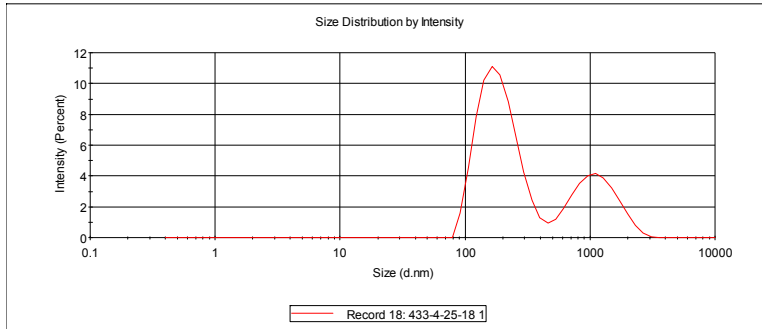


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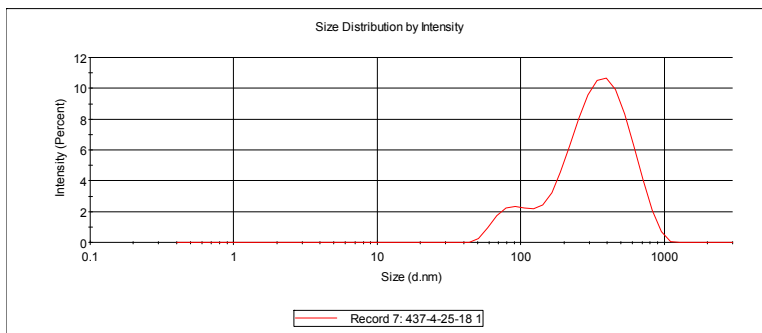


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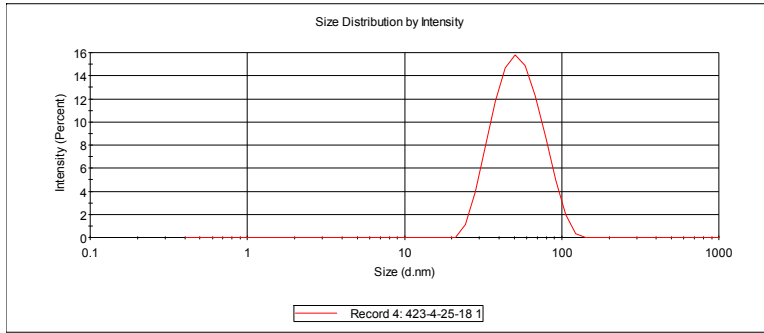


Table 1 entry 5 and Table S1 entry S5

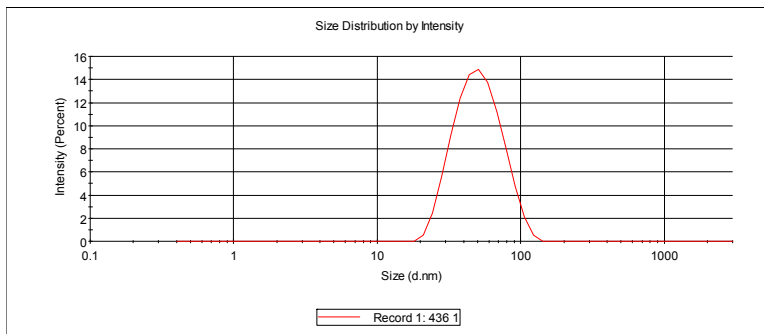


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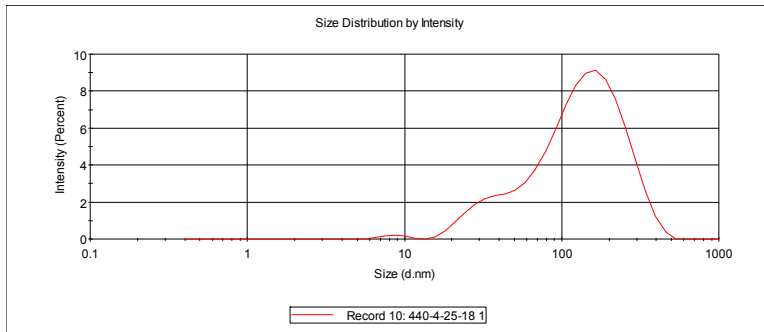


Table 1 entry 7, Table 2 entry 2 and Table S1 entry S1

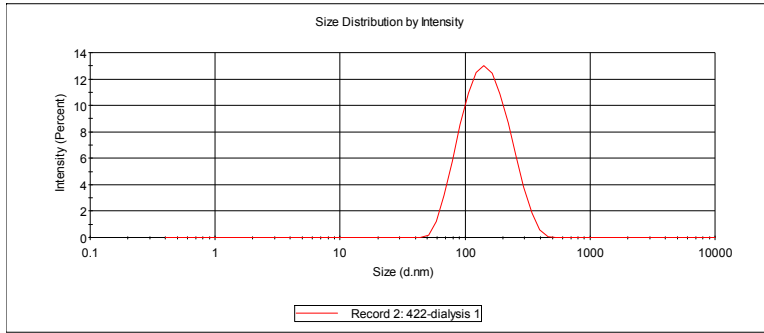


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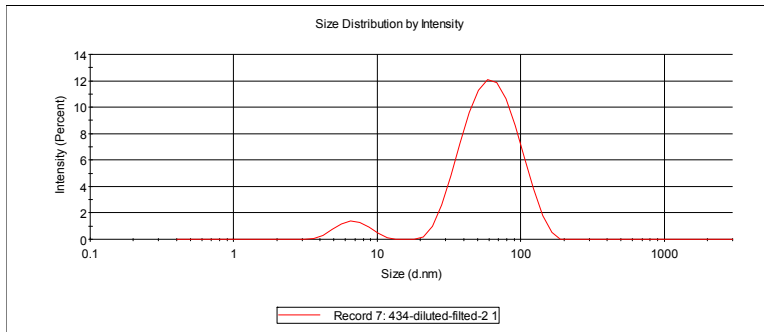


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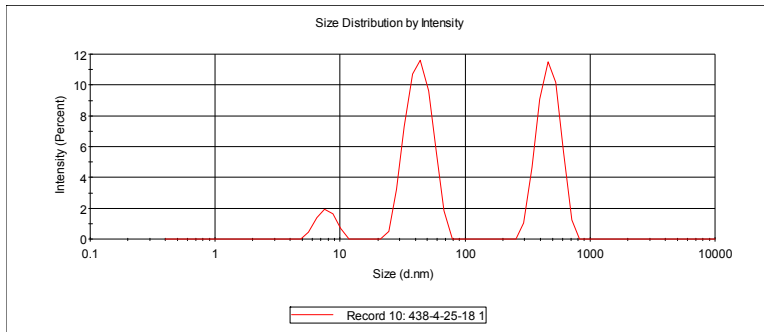


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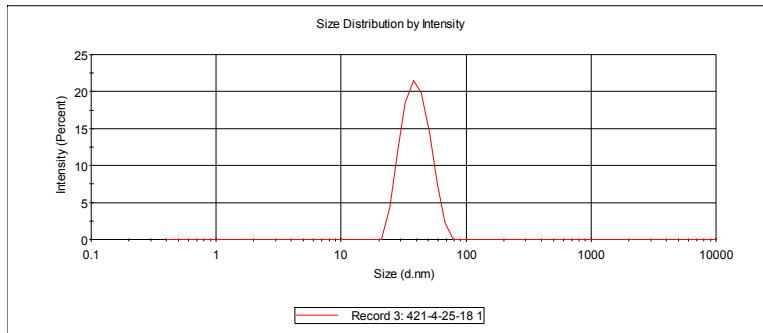


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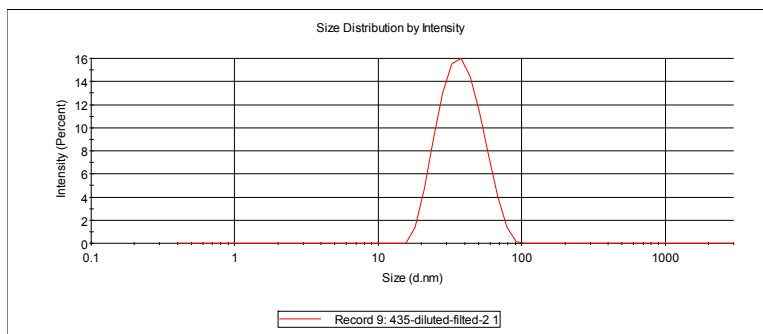


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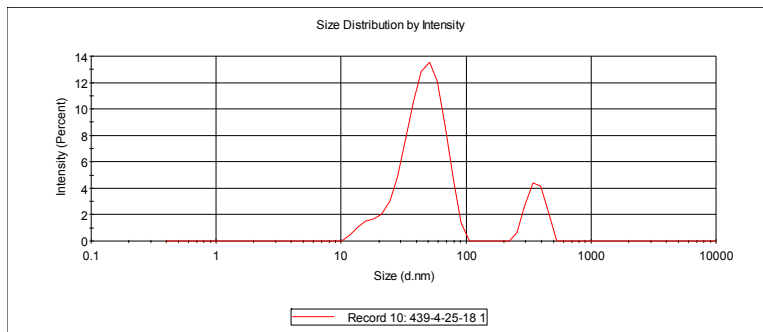


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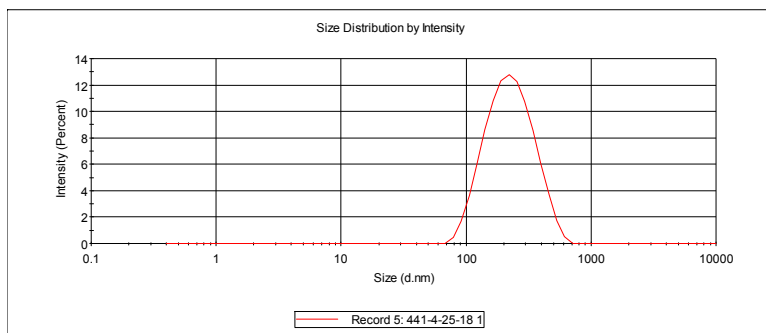


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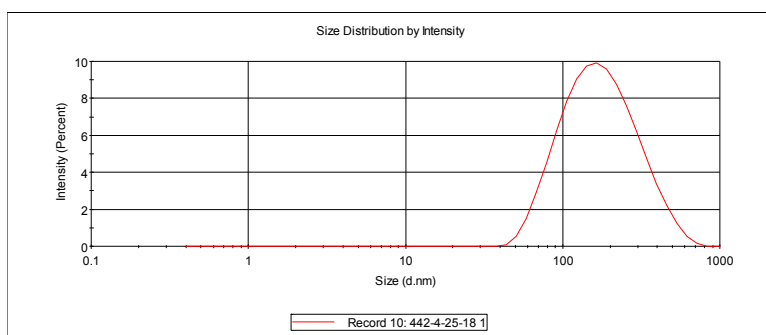


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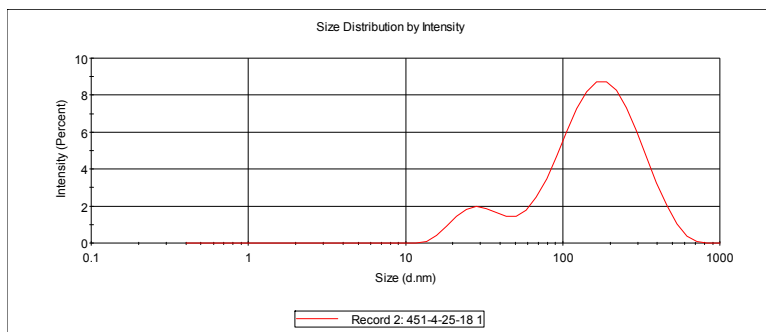


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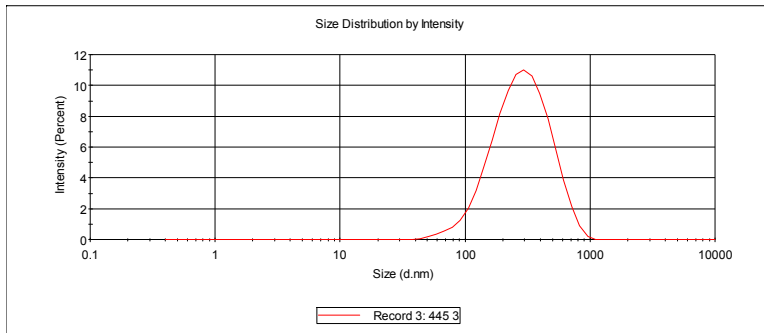


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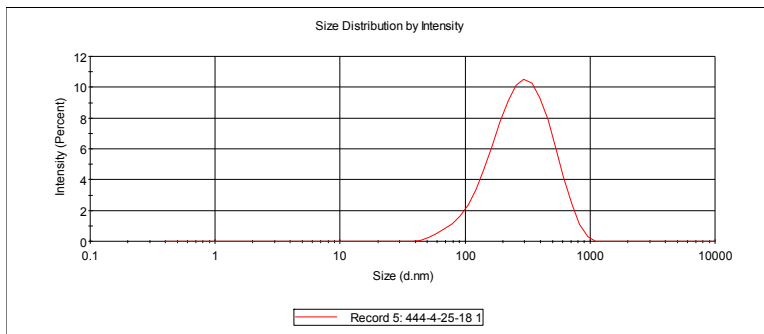


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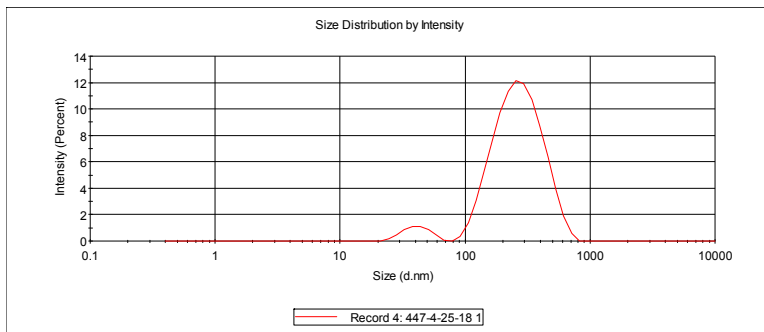
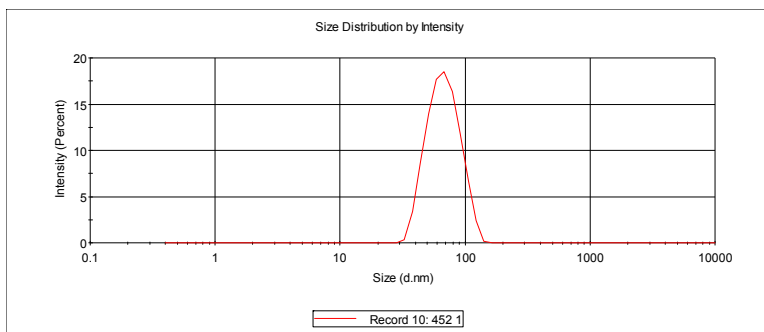
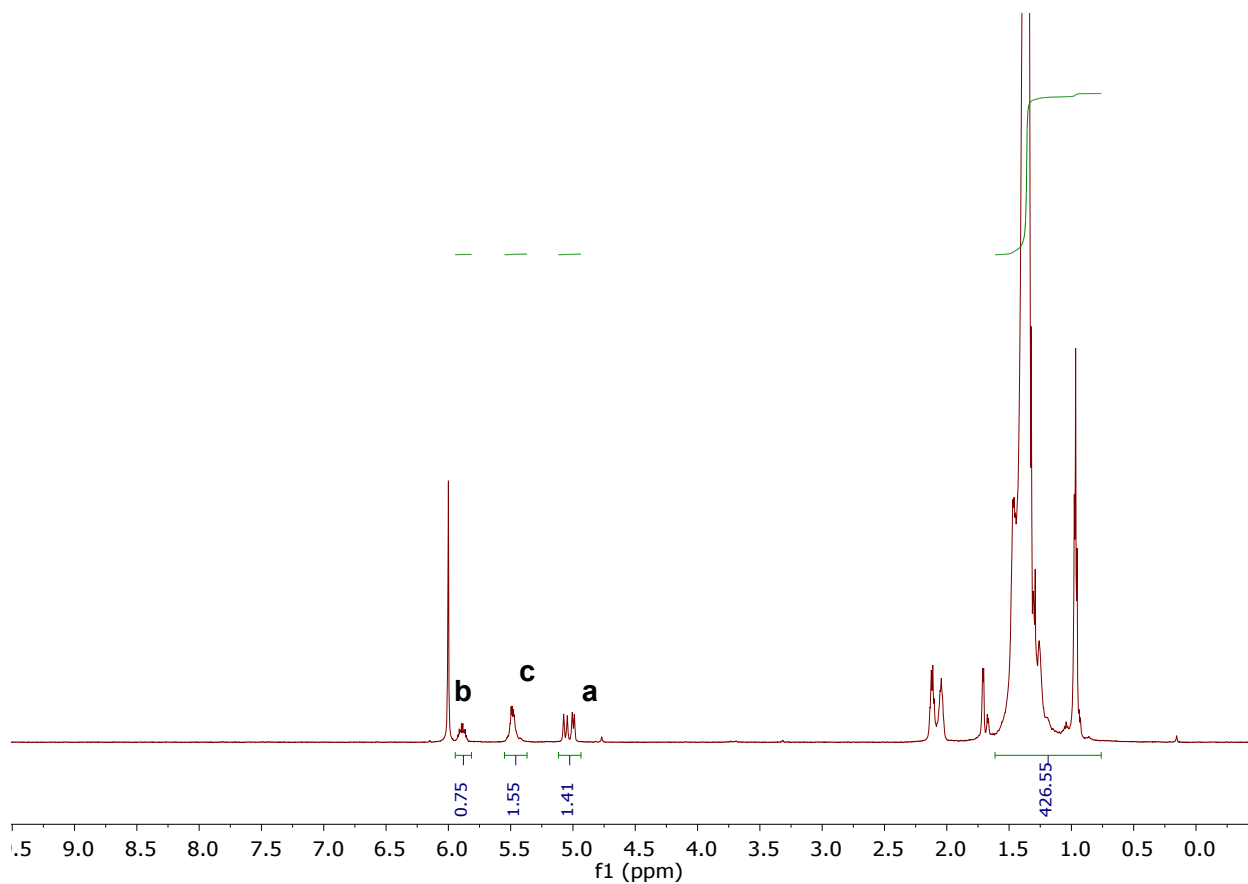
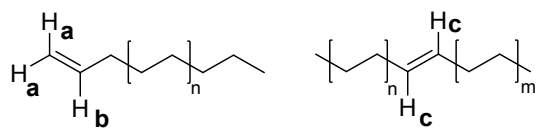


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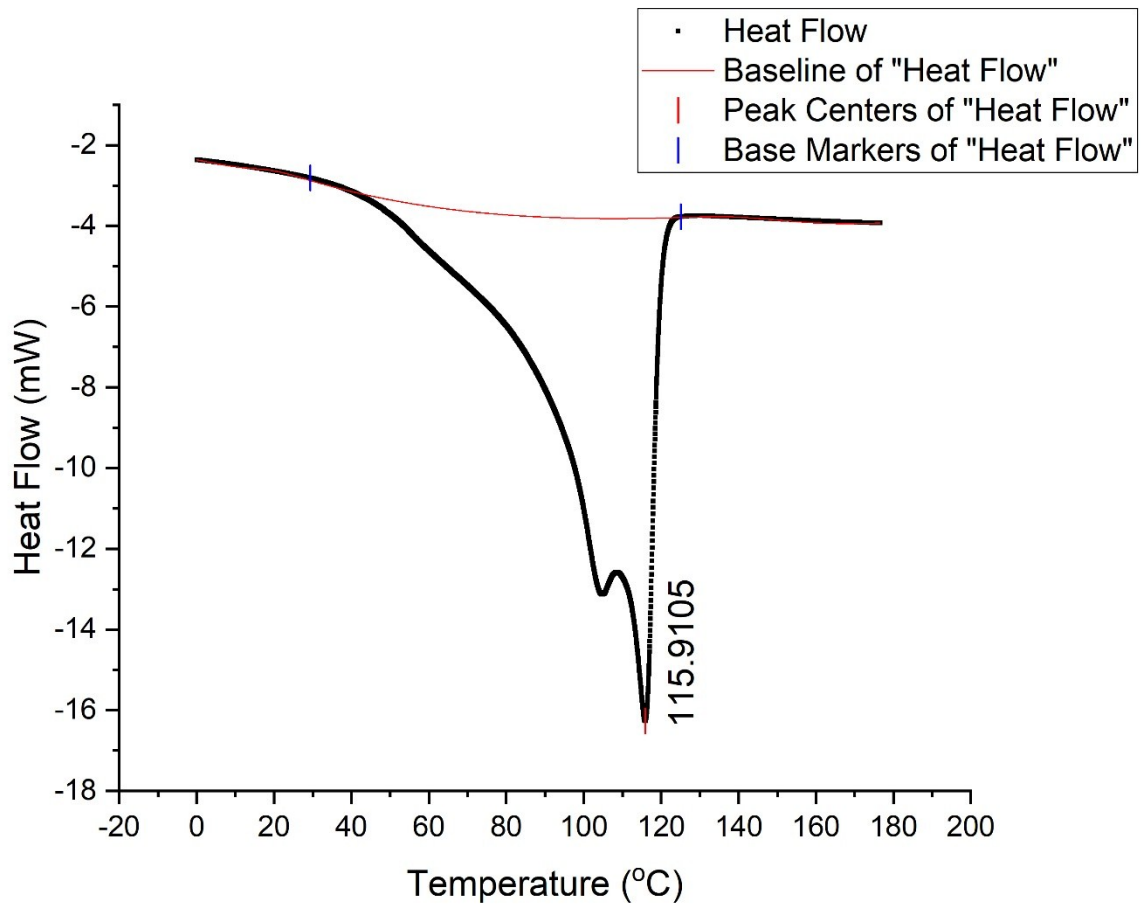


3. Polyethylene NMR analysis



Representative 1H NMR (600 MHz, in $C_2D_4Cl_2$, at 120°C) of the polyethylene

4. Polyethylene DSC analysis



Representative DSC of polyethylene made in water

5. UV data

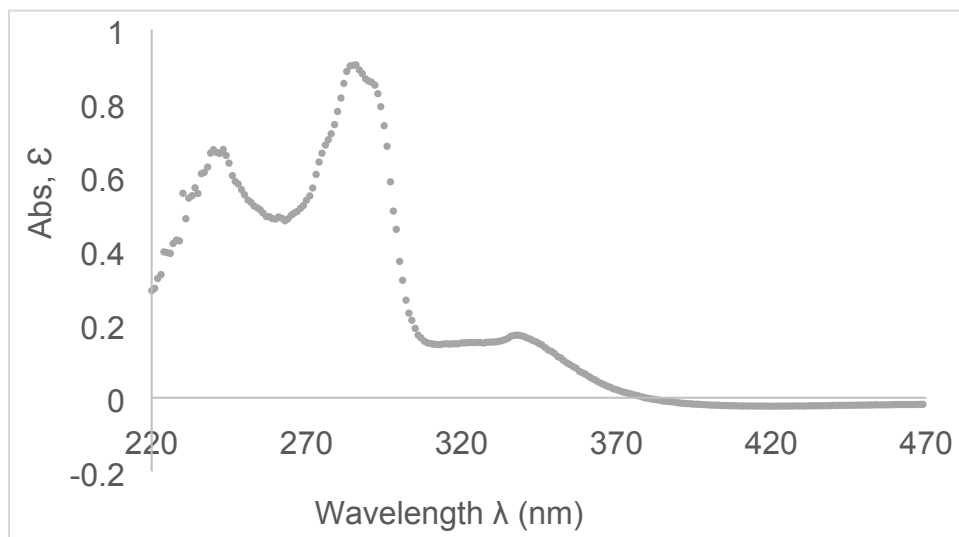


Figure S2. UV spectrum of 1-Pd-DMSO in water/Rhodafac®

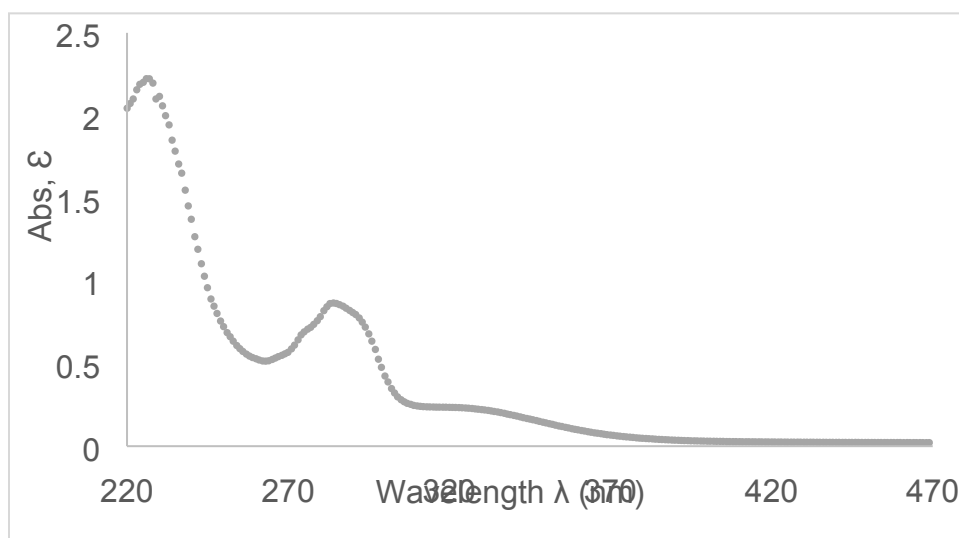


Figure S3. UV spectrum of 1-Pd-DMSO in water

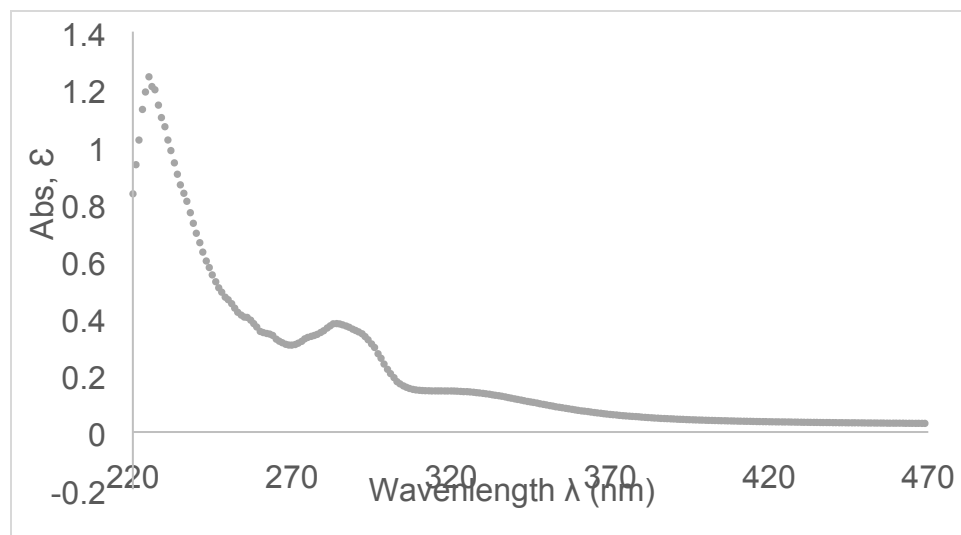


Figure S4. UV spectrum of 1-Pd-pyr in water

6. Calculations

- Correlation $\frac{m_{PE}^{latex}}{m_{PE}^{coag}}$

$$cat_{TOT} = cat_{latex} + cat_{coag}$$

$$mPE_{latex} = TOF_{latex} * cat_{latex}$$

$$mPE_{coag} = TOF_{coag} * cat_{coag}$$

$$cat_{latex} = cat_{TOT} - cat_{coag}$$

$$mPE_{latex} = TOF_{latex} * (cat_{TOT} - cat_{coag})$$

$$cat_{coag} = cat_{TOT} - \frac{mPE_{latex}}{TOF_{latex}}$$

$$mPE_{coag} = TOF_{coag} * \left(cat_{TOT} - \frac{mPE_{latex}}{TOF_{latex}} \right)$$

$$mPE_{coag} = -\frac{TOF_{coag}}{TOF_{latex}} mPE_{latex} + TOF_{coag} * cat_{TOT}$$

- Volume of 1 particle

$$MW = 2800 \text{ g/mol} \quad N_{av} = 6.02 \cdot 10^{23}$$

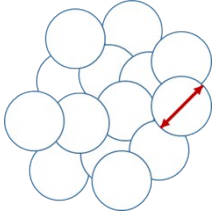
$$m_{1molecule} = \frac{MW}{N_{av}}$$

$$m_{1molecule} = \frac{2800}{6.02 \cdot 10^{23}} = 4.65 \cdot 10^{21} \text{ g}$$

$$\rho_{PE} = 0.93 \text{ g/cm}^3 = 0.93 \cdot 10^{-21} \text{ g/nm}^3$$

$$Volume_{1molecule} = \frac{m_{1molecule}}{\rho_{PE}} = 5 \text{ nm}^3$$

- Particle Volume from TEM data

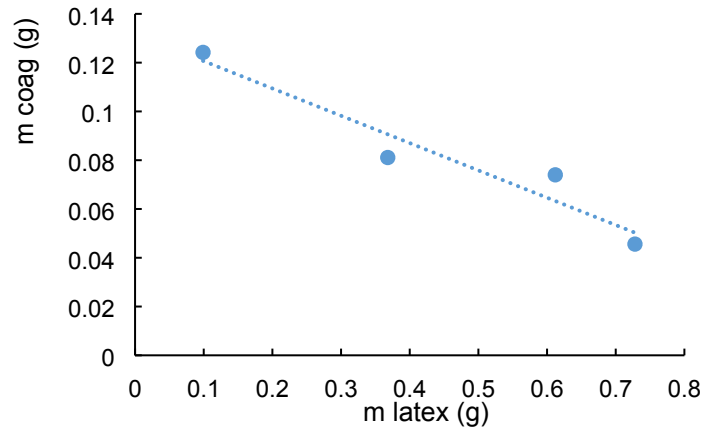


diameter $d = 4.8 \text{ nm}$ radius $r = 2.4 \text{ nm}$

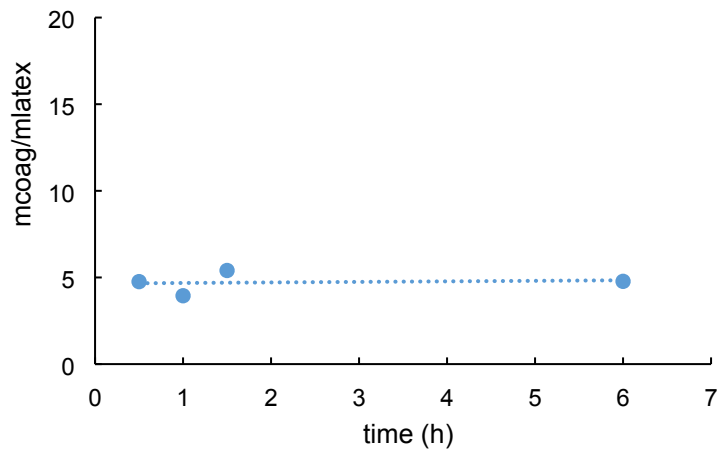
$$V_{TEM} = \frac{4}{3} \pi r^3 = 10.9 \text{ nm}^3$$

7. Data plots

a. Correlation of coagulate PE and latex PE formed



b. $\frac{m_{PE}^{latex}}{m_{PE}^{coag}}$ ratio over time



8. References

- (1) Guironnet, D.; Roesle, P.; Rünzi, T.; Göttker-Schnetmann, I.; Mecking, S. Insertion Polymerization of Acrylate. *J. Am. Chem. Soc.* **2009**, *131* (2), 422–423.
- (2) Zhang, D.; Guironnet, D.; Göttker-Schnetmann, I.; Mecking, S. Water-Soluble Complexes $[(\kappa^2\text{-}P,O\text{-Phosphinesulfonato})\text{PdMe(L)}]$ and Their Catalytic Properties. *Organometallics* **2009**, *28* (14), 4072–4078.