# **Supplementary Materials**

# Catalysed Tandem Dehydrochlorination-Hydrogenation of PVC towards valorisation of chlorinated plastic waste

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### **Supplementary information**

# 1. ATR FTIR analysis of polymers

Benchtop ATR FTIR was used as a method to analyze solid reaction products. Spectra are displayed in transmission, for which a normalization is done, thereby assigning the most intense vibrational peak as 0% transmission. Firstly, as illustrated in **figure S1.**, different polymers containing variable content of Cl were characterized by the vibrational peaks. PVC displays more intense Cl-related vibrational peaks, while chlorinated polyethylene (CPE, with 25 m% Cl) and PE (0 m% Cl) display predominantly intense peaks for CH<sub>2</sub>-related vibrations. The assigned peaks for each polymer are:

PVC (in cm<sup>-1</sup>): 2993 (w,  $v_s$  CHCl), 2950 (w,  $v_{as}$ CH<sub>2</sub>), 2843 (w,  $v_s$ CH<sub>2</sub>), 1425 (s,  $\delta$ CH<sub>2</sub>), 1329 (w,  $\delta$ CH<sub>2</sub>), 1252 (s,  $\delta$ CHCl), 1077 (s, C-C stretch), 969 (s, CH<sub>2</sub>-rocking), 861 (w) , 829 (w), 691 (m, C-Cl stretch), 608 (s, C-Cl stretch).

CPE (in cm<sup>-1</sup>): 2911 (s,  $v_{as}$ CH<sub>2</sub>), 2845 (s,  $v_{s}$ CH<sub>2</sub>), 1425 (s,  $\delta$ CH<sub>2</sub>), 1252 (m,  $\delta$ CHCl), 1077 (m, C-C stretch), 718 (s, CH<sub>2</sub>-rocking).

PE (in cm<sup>-1</sup>): 2913 (s,  $v_{as}$ CH<sub>2</sub>), 2846 (s,  $v_{s}$ CH<sub>2</sub>), 1461 (s,  $\delta_{as}$ CH<sub>2</sub>), 718 (s, CH<sub>2</sub>-rocking).

These peaks were used as references for peaks of reaction products. Since the reaction products display various degrees of dehydrochlorination-hydrogenation.



Figure S1. ATR FTIR of virgin polymers; PVC (green), chlorinated PE with 25 m% of Cl (blue) and PE (red).

### 2. Solid state <sup>13</sup>C NMR

Magic angle spinning (MAS) and Cross-Polarization Magic angles spinning (CP-MAS) solid-state NMR experiments were performed with a Varian Inova 500 WB system and a 4 mm Chemagnetics probe at 25°C. Proton decoupling was used in the detection of <sup>13</sup>C NMR signals of virigin PVC and product samples, which were spun at 15 kHz about the magic angle to perform the experiments. 90° pulse widths for carbon and proton were calibrated to 3  $\mu$ s and 4  $\mu$ s, respectively, and the contact time was set to 3.5 ms. The repetition delay was 20 s and 1024 scans were accumulated. The spectral window was 40 kHz and the FID had a duration of 0.04 s recorded with 1600 complex points. The FID was zero-filled to 8192 points before performing the FFT and a linear broadening of 15 Hz was used as apodization. The chemical shifts referenced to an adamantane external standard. In the MAS spectrum, a peak at 110 ppm was related to a background signal originating from the probe.

Solid state NMR (**Figure S2**) was used to elucidate the solid polymer product structure (product of 1 mmol PVC, 0.85 mmol Bu<sub>4</sub>PCl, 0.5 mol% H(CO)Rh(PPh<sub>3</sub>)<sub>3</sub> in 2-butanone for 2 h under 20 bar H<sub>2</sub> at 180°C). Magic angle spinning (MAS) shows all types of carbon atoms in the structure, with Cross-Polarisation (CP)-MAS only showing carbons that contain protons, with enhanced sensitivity. The MAS spectrum demonstrates a quaternary C peak at 67 ppm.



**Figure S2.** Solid state magic angle spinning (MAS) and cross-polarisation (CP)-MAS  $^{13}$ C-NMR spectra of tandem dehydrochlorination-hydrogenation product. (product of 1 mmol PVC, 0.85 mmol Bu<sub>4</sub>PCl, 0.5 mol% H(CO)Rh(PPh<sub>3</sub>)<sub>3</sub> in 2-butanone for 2h under 20 bar H<sub>2</sub> at 180°C). Marked peak at 67 ppm in MAS are quaternary carbon atoms.

# 3. Liquid NMR elucidation of product

The structure of the product (product of 1 mmol PVC, 0.85 mmol Bu<sub>4</sub>PCl, 0.5 mol% H(CO)Rh(PPh<sub>3</sub>)<sub>3</sub> in 2butanone for 2 h under 20 bar H<sub>2</sub> at 180°C) was further elucidated by liquid NMR. Firstly, distortionless enhancement by polarisation transfer-135 (DEPT-135) showed the bonding properties of all carbons in the <sup>13</sup>C spectrum. By this CHCl groups, had clear shifts in the range of (64-58 ppm), while various types of CH<sub>2</sub> groups are detected in the range of 47-26 ppm (**figure S3**).

# **DEPT-135**



**Figure S3.** Liquid <sup>13</sup>C-NMR ( $d^{8}$ -THF, 400 MHz) and Distortionless enhancement by polarisation transfer (DEPT) spectra of tandem dechlorinated product. (product of 1 mmol PVC, 0.85 mmol Bu<sub>4</sub>PCl, 0.5 mol% H(CO)Rh(PPh<sub>3</sub>)<sub>3</sub> in 2-butanone for 2h under 20 bar H<sub>2</sub> at 180°C ). In DEPT-135, CH and CH<sub>3</sub> appear as positive peaks while the CH<sub>2</sub> peaks are negative peaks.

Further proof for the <sup>13</sup>C-<sup>1</sup>H NMR shift correlation between groups in the polymer product backbone was seen by heteronuclear Single Quantum Coherence-DEPT (HSQC-DEPT, **Figure S4**.), by which the <sup>1</sup>H-NMR shift of 5.5 ppm (=CH-groups) correlates perfectly for double bonded groups at 130 ppm (<sup>13</sup>C shift). CHCl groups of the VC-VC units correlate at (4.6-4.3 ppm (<sup>1</sup>H)- 58 ppm (<sup>13</sup>C)), while CHCl groups (E-VC-E units) correlate at slightly different shifts (3.9 ppm (<sup>1</sup>H)- 63-60 ppm (<sup>13</sup>C)).



**Figure S4.** HSQC-DEPT135 NMR spectrum of Tandem dechlorination-hydrogenation product (400 MHz,  $d^8$ -THF). Assigned boxes indicate the correlation of <sup>1</sup>H-<sup>13</sup>C shifts. (product of 1 mmol PVC, 0.85 mmol Bu<sub>4</sub>PCl, 0.5 mol% H(CO)Rh(PPh<sub>3</sub>)<sub>3</sub> in 2-butanone for 2h under 20 bar H<sub>2</sub> at 180°C ).

#### 4. Determination of the degree of dechlorination

The degree of dechlorination was determined by liquid <sup>1</sup>H-NMR (d<sup>8</sup>-THF, 400 MHz), for which proton integration is used to determine the relative fraction of the different types of carbon groups on the polymer chain. As an example for the calculation of the degree of dechlorination procedure. The spectrum of PVC is compared with a polymer product. The spectrum of PVC (**Figure S5**) displays three peaks at 4.7-4.3 ppm, that represent CHCl groups (Vinyl chloride units in polymer), and integrate for 1 proton in the spectrum, while  $CH_2$ -groups (that are adjacent to CHCl in vinyl chloride units) with a shift of 2.4-2.0 ppm, are 2.00 by integration. Hence, this means the PVC backbone consists of equimolar amounts of  $CH_2$ :CHCl groups, as is expected from the molecular structure. This 1:1 ratio or 50% CHCl groups equals a dechlorination degree of 0%.



**Figure S5.** <sup>1</sup>*H*-*NMR* ( $d^{8}$ -*THF*, 400 MHz) of unaltered PVC with CHCl (4.7-4.3 ppm) in equimolar ratio as CH<sub>2</sub> (2.4-1.9 ppm). In agreement with the theoretical number of protons integrations are 2:1 in intensity (CH<sub>2</sub>:CHCl).

The <sup>1</sup>H-NMR spectrum of a polymer product (**Figure S6**) (product after 1 h reaction, with 1.0 mol%  $H(CO)Rh(PPh_3)_3$  and 0.85 eq.  $Bu_4PCl$  at 180°C), shows several more peaks for =CH-groups (5.5 ppm, integration value 1.00) CHCl groups (VC-VC sequences) (4.6-4.1 ppm, integration value 2.34) and CHCl groups in ethylene (E) sequences (E-VC-E) (3.9 ppm). Additionally, the two types of CH<sub>2</sub>-groups, that are either beside CHCl on the chain (in E-VC 2.4-2.0 ppm, integration value 4.91), or in a sequence of ethylene CH<sub>2</sub> groups (E-E at 1.6-1.3 ppm, integration value 17.61) are summed to give a total integration value of 22.50. The determined integrals are subsequently normalised by dividing these values by the theoretical number of each carbon group (1H for CHCl and CH=CH, 2H for CH<sub>2</sub>). Subsequently the normalised integrals are summed (summed normalised integral value is 14.81), and the fraction of each group is determined by dividing its normalised integral by the sum of the normalised integral value. For instance, the fraction of CH=CH groups giving 3.3% double bonds on the polymer backbone. Additionally, the normalised fraction of CHCl groups in this spectrum is: CHCl in VC-VC: (2.34/14.81) x 100 % = 15.7 %, CHCl in E-VC-E: (0.51/14.81) x 100% = 3.3%, with thereby a total fraction of CHCl groups of 19%. The fraction of CH<sub>2</sub> groups

is calculated by dividing 11.25 (=22.50/2) by the summed normalised integral value, hence the CH2 fraction is (11.25/14.81)\*100 % = 74.5%.

For calculation the degree of dechlorination is defined as:

100 % - (Number of residual CHCl)/(Number of initial CHCl groups)

Hence, with 50% for initial CHCl groups, a residual fraction of 19% annotates a degree of dechlorination of 62% (100% - (19%/50%)).



**Figure S6.** <sup>1</sup>H NMR ( $d^8$ -THF, 400 MHz) of polymer product displaying peaks for double bonds (5.5 ppm), CHCl-groups (in VC-VC, 4.6 – 4.1 ppm), CHCl-groups (in E-VC-E, 3.9 ppm) and CH<sub>2</sub> groups adjacent to CHCl (2.4-2.0 ppm) and CH<sub>2</sub>-groups vinyl chloride units (VC, 1.6-1.3 ppm). The integration values of the CH<sub>2</sub> groups is summed to calculate the fraction of CH<sub>2</sub>-groups and the degree of dechlorination. (After 1 h reaction, with 1 mol% H(CO)Rh(PPh<sub>3</sub>)<sub>3</sub> and 0.85 eq. Bu<sub>4</sub>PCl at 180°C).



Chemical shift (ppm)

:

**Figure S7.** <sup>1</sup>*H*-NMR spectra (d<sup>8</sup>-THF, 400 MHz) of unreacted PVC (green) and tandem dechlorinationhydrogenation products of PVC by 0.85 mmol ionic liquid after 2h, with RhCl<sub>3</sub>.H<sub>2</sub>O catalyst loadings; 2.0 mol% (A), 1.0 mol% (B), 0.5 mol% (C). Percentages indicate the fraction of CH=CH groups (2 x amount of double bonds per 100 C) and CHCl groups in the product, determined by integration of the NMR peaks.

# 5. Reaction to determine crosslinking with added HCl

PVC (1 mmol based per monomer unit with molar mass of 62.6 g/mol , 62.5 mg),  $Bu_4PCI$  (0.85 mmol, 250 mg) and  $H(CO)Rh(PPh_3)_3$  (2 mol%, 18.4 mg) were brought into a glass liner. Thereafter, 1-butanone (1 mL) and HCl in dioxane solution (2 mmol, 4.0 M, 0.5 mL) were added to the glass liner, which was then placed inside the reactor. Subsequently, the reactor was sealed and purged twice with N<sub>2</sub>-gas before filling it with 20 bar of H<sub>2</sub>-gas. The reaction mixture was then stirred (750 rpm) at elevated temperature (100-180°C). After heating for the designated time, the reaction was quenched by cooling the reactor in an ice bath. After 30 minutes reaction, the obtained product was still dissolved in the solvent. This product was purified by first precipitation with water/ethanol, decantation of solvent and subsequent dissolution step to remove residues was used for purification. The <sup>1</sup>H-NMR of the product after 30 minutes showed 17% dechlorination. The product after 1h, was precipitated in the butanone and had a black appearance (**Figure S8**). This product had limited solubility in solvents, thereby impeding NMR analysis.



**Figure S8.** Picture of reaction product in solvent after 1h, with added HCl solution. (1 mmol PVC reaction with 0.85 eq.  $Bu_4PCl$ , 2 mol% H(CO)Rh(PPh<sub>3</sub>)<sub>3</sub>, in 1 mL butanone and added 0.5 mL HCl solution in dioxane (2 mmol, 4 M).

# 6. XAS supporting info

Entry	Rh-precursor	IL	Description
1	H(CO)Rh(PPh3)3	Bu <sub>4</sub> PCl	$H(CO)Rh(PPh_3)_3$ in CI-IL before reaction with PVC
2	H(CO)Rh(PPh3)3	Bu <sub>4</sub> PCl	$H(CO)Rh(PPh_3)_3$ in Cl-IL after reaction with PVC
3	H(CO)Rh(PPh3)3	Bu <sub>4</sub> PBr	$H(CO)Rh(PPh_3)_3$ in Br-IL before reaction with PVC
4	H(CO)Rh(PPh3)3	Bu <sub>4</sub> PBr	$H(CO)Rh(PPh_3)_3$ in Br-IL after reaction with PVC
5	RhCl3	Bu4PCl	$RhCl_3$ in Cl-IL after reaction with PVC
6	RhCl₃	/	RhCl₃ Reference
7	Rh foil	/	Rh foil Reference

Reaction conditions: 0.02 mmol Rh catalyst, 0.85 mmol  $Bu_4PX$  (X = Cl<sup>-</sup>/Br<sup>-</sup>), 1 mmol PVC, stirred for 2h under 20 bar  $H_2$  at 180°C. Solid samples of Rh embedded in ionic liquid were obtained after evaporation of the butanone reaction solvent.

#### 7. Ionic liquid reuse and catalyst stability



**Figure S9.** Characteristics of precipitated product after multiple tandem dehydrochlorination-hydrogenation reaction cycles. Dehydrochlorination activity diminishes gradually after every cycle, while Rh-catalyst activity remains high (1 double bond per 100 C maximally remains, after every cycle). Reactions were performed with a fresh load of PVC for every cycle (1 mmol), and with the ionic liquid/Rh-catalyst recovered in solvent (0.85 eq.  $Bu_4PCl$ , 1 mol%  $H(CO)Rh(PPh_3)_3$ , 1 mL butanone, heating at 180°C for 2 h under 20 bar  $H_2$ ).

The stability of the Rh-catalyst under the applied reaction conditions was verified by a recycling experiment (**Figure S9**). For this, the reaction was initially performed with 0.85 eq. Bu<sub>4</sub>PCl, 1 mol% H(CO)Rh(PPh<sub>3</sub>)<sub>3</sub> in 2-butanone (1 mL). During each reaction, the polymer product precipitated in the solvent, after which it was removed and new virgin PVC (1 mmol) was added to the reaction mixture. After each cycle, the recovered product was 40-50 % of the mass of the virgin PVC added, which signifies that the dechlorination happens to large extent since PVC contains 57% of Cl. A mass loss of 50% is expected for complete conversion to a more saturated, PE-like polymer. The observed dechlorination degree of the recovered products (determined by <sup>1</sup>H-NMR) shows that quite extensive dechlorination still happens in the third cycle, but that the dissolved ionic liquid gradually loses some activity in each cycle. The homogeneous Rh complex on the other hand, retains its activity over three reaction cycles, since only between 0 and 1% double bonds on the polymer backbone are detected after every reaction. As a qualitative method, FTIR confirmed the highly saturated nature of the polymer products obtained after each reaction (**Figure S10**).



**Figure S10.** ATR FTIR spectra of (A) PVC and reaction products after ionic liquid and catalyst stability experiment over three cycles with; (B)  $1^{st}$  cycle, (C)  $2^{nd}$  cycle, (D)  $3^{rd}$  cycle. For each cycle,  $Bu_4PCI$  (0.85 eq.,  $H(CO)Rh(PPh_3)_3$  (1 mol%) and butanone solvent (1 mL) were reused from the previous reaction. Converted PVC (1 mmol) was characterized after isolation from the reaction mixture.