Supplementary materials

Conversion of diverse Post-consumer PVC waste materials to PE via dual catalytic Tandem Dehydrochlorination-Hydrogenation

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1. Screening of metal salts for tandem dehydrochlorination-hydrogenation of PVC

Initial screening for conditions for PVC conversion, involved changing the employed metal salt catalyst that is used to elicit HCl release from PVC. Employing different metals for the tandem process (**Table S1**) showed some interesting aspects of the dual catalyst workings. Since a Rh-catalyst demonstrated an effective means for hydrogenation of the products when using ionic liquid promoters for dehydrochlorination[1], its applicability for this $ZnCl_2$-catalysed approach was explored. Although the novel Zn-based system with complete dechlorination (**Entry 1**) led to a very low molecular weight polymer product, combining this with a Rh-catalyst for the hydrogenation step led to charring of the product (**Entry 2**). While a $ZnBr_2$-Ru combination did show excellent activity (**Entry 3**), substituting the salt for $Zn(OAc)_2$ led to charring of the product, probably due to the negative effect of the acetate counter-ions on the hydrogenation catalyst. Different metal halides based on Mg (**Entries 5-6**), Cu (**Entry 7**) and Fe (**Entry 8**) gave no added activity for dechlorination. On the contrary, a significant increase in the molar mass of the polymer products was observed by using these metals, which was observed by GPC. Based on the Number average molar mass of the products, corrected for the molar mass of monomer units of PVC (62 g/mol) or PE (28 g/mol), a strong decrease in the degree of polymerization (DP) was observed using Zn halides, in stark contrast to the other metals, for which either charring occurred (*insoluble products in **Table S1**) or the formation of soluble products with ~60% increase in the DP compared to PVC.

Entry	Metal salt (0.2 mmol)	Hydrogenation catalyst (1.0 mol%)	Degree of dechlorination (%)[a]	Average Molar masses (M_n/M_w in g/mol)[b]	Relative change in Degree of depolymerisation (M_n based)[b]
1	$ZnCl_2$	$HCl(CO)Ru(PPh_3)_3$	100	2400/5080	-92%
2	$ZnCl_2$	**$H(CO)Rh(PPh_3)_3$**	*	*	*
3	$ZnBr_2$	$HCl(CO)Ru(PPh_3)_3$	100	2400/5080	-92%
4	$Zn(OAc)_2$	$HCl(CO)Ru(PPh_3)_3$	*	*	*
5	$MgCl_2$	$HCl(CO)Ru(PPh_3)_3$	45	79600/156000	60%
6	$MgBr_2$	$HCl(CO)Ru(PPh_3)_3$	45	79600/156000	60%
7	$CuCl_2$	$HCl(CO)Ru(PPh_3)_3$	7	103000/170000	62%
8	$FeCl_3$	$HCl(CO)Ru(PPh_3)_3$	*	*	*

Table S1. *Screening of different metal salts, combined with the hydrogenation catalyst, in the tandem dehydrochlorination-hydrogenation conditions. Reaction conditions: 1.0 mmol LMW-PVC, 0.2 mmol metal salt and 0.01 mmol hydrogenation catalyst in 1 mL methyl cyclohexanecarboxylate solvent, stirred at 180°C under 20 bar H_2, for 16h. [a]Degree of dechlorination determined by ^1H-NMR. [b] Number average (M_n) and Weight average (M_w) Molar mass determined by GPC of products in THF. *Insoluble products (for which ^1H-NMR and GPC characterization were not possible).*

2. Determination of the extent of dechlorination

2.1 ^{1}H-NMR of virgin PVC and PE

As references for the starting material and the reaction product after tandem dehydrochlorination-hydrogenation, the ^{1}H-NMR spectra of virgin PVC and low-density polyethylene (LDPE) were recorded. For this, 5 mg of the virgin polymer samples was dissolved at 50°C in d^8-THF before ^{1}H-NMR measurements at room temperature (d^8-THF, 400 MHz). In the spectrum of PVC (**Figure S1, A**), peaks at 4.7-4.3 ppm originate from the CHCl groups in the structure, while the α-CH$_2$ groups adjacent to these give rise to a broad peak at 2.4-2.0 ppm. The spectrum of low molecular weight-LDPE (**Figure S1, B**) shows a major peak at 1.3 ppm, which originates from the -CH$_2$-groups of the polymer backbone. Additionally, a low intense peak at 0.9 ppm marks the CH$_3$ end groups of the polymer.
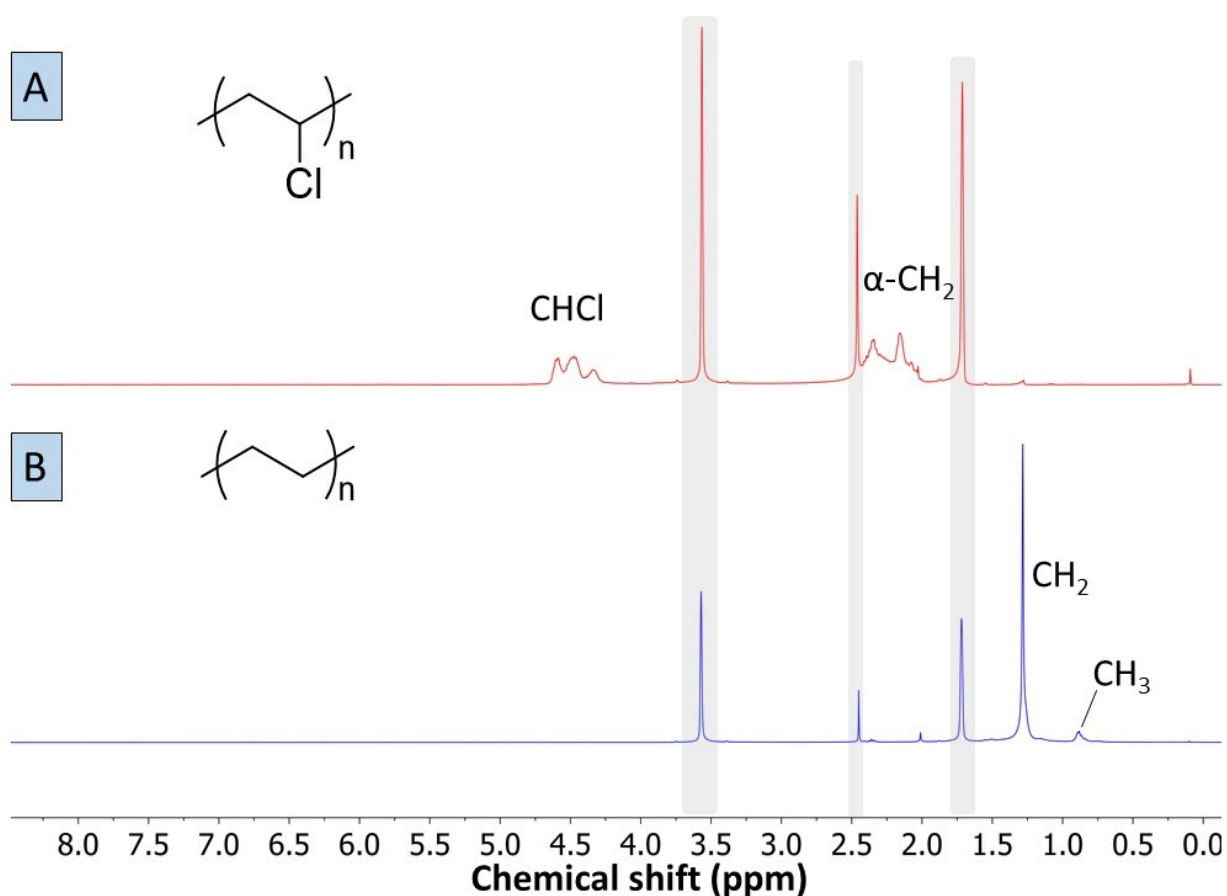
**Figure S1.** ^{1}H-NMR spectra (400 MHz, d^8-THF) of virgin polymers. (A) for PVC: CHCl (4.7-4.5 ppm) and CH$_2$ (2.4-2.1 ppm). (B) for PE: CH$_2$ (1.3 ppm) and CH3 (0.9 ppm). Residual solvent peaks are marked in grey boxes for THF; at 3.57 ppm (CH$_2$) and 1.77 ppm (CH$_2$), and for H$_2$O at 2.47 ppm (OH).

## 2.2 Determination of degree of dechlorination by liquid ^{1}H-NMR

Liquid ^{1}H-NMR was used to determine the degree of dechlorination of polymer products, to quantify the extent of the tandem dehydrochlorination-hydrogenation reactions. Proton integration was performed to determine the relative fraction of groups in the polymer backbone. This section demonstrates the procedure for determination of the degree of dechlorination, which is defined as: 100% (1 − (fraction of CHCl groups in products)/(fraction of CHCl in PVC)). To exemplify the method, a comparison of spectra of virgin PVC, partially dechlorinated polymer and completely dechlorinated product is made:

The spectrum of PVC (**Figure S2**) displays three peaks at 4.7- 4.3 ppm, which represent CHCl groups and integrate for 1.00 proton in the spectrum, while α-CH$_2$-groups (adjacent CH$_2$-groups of CHCl) with a shift of 2.4-2.0 ppm, integrate for 2.05. Hence, this indicates a molar ratio of 50% CHCl (1.00/ 1 theoretical proton = 1) and 50% CH$_2$ (2.05/ 2 theoretical protons = 1.0), as is expected from the PVC structure (1:1 ratio of CHCl:CH$_2$). This 1:1 ratio or 50% CHCl groups equals a dechlorination degree of 0% since (100% (1 − (50%/50%)) =0%.
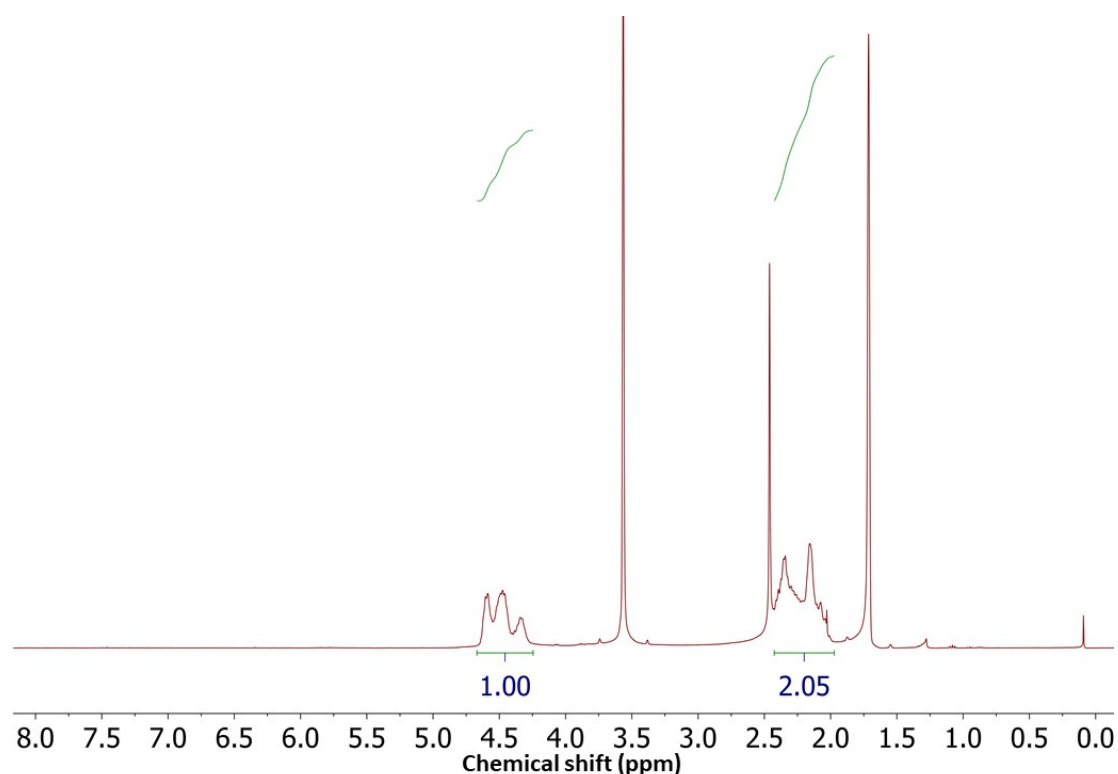
**Figure S2.** ^{1}H-NMR spectrum of PVC (d^8-THF, 400 MHz). Integration of peaks corresponding to CHCl and CH$_2$, demonstrates a molar ratio of 1:1 of these groups in the polymer backbone.

The ^{1}H-NMR spectrum of a reaction product (CDCl$_3$, 400 MHz), after tandem dehydrochlorination-hydrogenation in THP displays various peaks (**Figure S3**) and shows partial, incomplete dechlorination. For quantification, peaks of all types of carbon atoms are integrated, after which the values are corrected for the theoretical number of protons (0.28/ 1 proton = 0.28 for =CH- (δ 5.4 ppm), 1.00/ 1 proton = 1.00 for CHCl (δ 4.7 – 4.0 ppm), 2.51/ 2 protons = 1.25 for α-CH$_2$ and 6.41/2 protons = 3.21 for CH$_2$. Hence the summed value of the corrected integrals is 0.28+1.00+1.25+3.21=5.74. From these values the relative fraction of the different carbon types yields 5% of =CH-Cl (0.28/5.74 = 4.88); 18% of CHCl (1.00/5,74 = 0.18); 22% of α-CH$_2$ (1.25/ 5.74 = 0.22); 56% of CH$_2$ (3.21/ 5.74 = 0.56). Therefore, the polymer product contains on average 2.5 double bonds per 100 carbon atoms ((5% of =CH-)/2 = 2.5). The dechlorination degree was determined according to the fraction of CHCl groups to be 100% (1 – (18%/50%))= 63%.
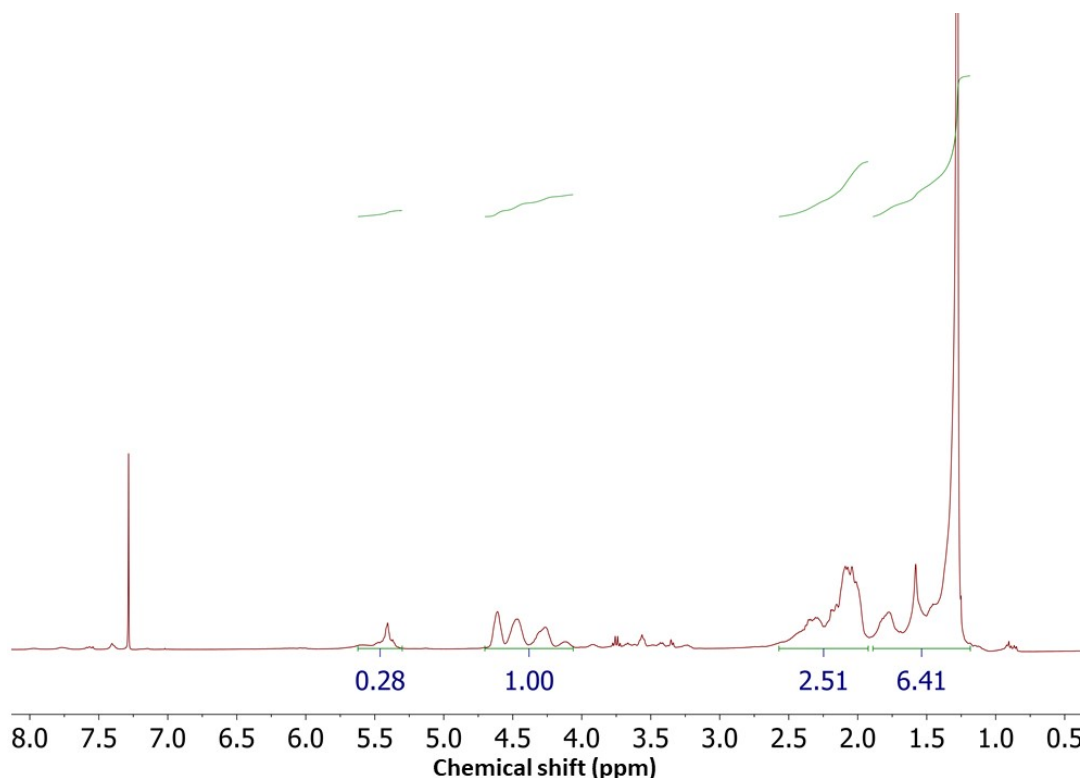
Figure S3. ^{1}H-NMR spectrum of polymer product with 63% dechlorination (CDCl$_3$, 400 MHz). (reaction conditions : 1.5 mmol PVC, 0.2 mmol ZnCl$_2$, 0.01 mmol HCl(CO)Ru(PPh$_3$)$_3$, 2 mL THP, reaction for 16h at 180°C under 20 bar H$_2$).

Finally, the ^{1}H-NMR spectrum (CDCl$_3$, 400 MHz) of a polymer product from reaction in methyl cyclohexanecarboxylate demonstrates complete reaction (**Figure S4**), with full conversion to PE material. For quantification, peaks of CHCl groups (δ 4.7-4.0 ppm) were negligible, but included in the calculation, while no residual =CH-groups were detected. CHCl-groups had a corrected integral value of 1.00/ 1 proton = 1.00, while CH$_2$-groups (δ 2.0-1.28 ppm) integrated for 103.84/2= 51.92. Hence, the total integration value was 1.0+51.92=52.92. From this, there was a fraction of 2% CHCl groups (1/52.92 = 0.18) and 98% CH$_2$-groups (51.92/52.92 = 0.98) in the polymer product, which asserts extensive dechlorination.
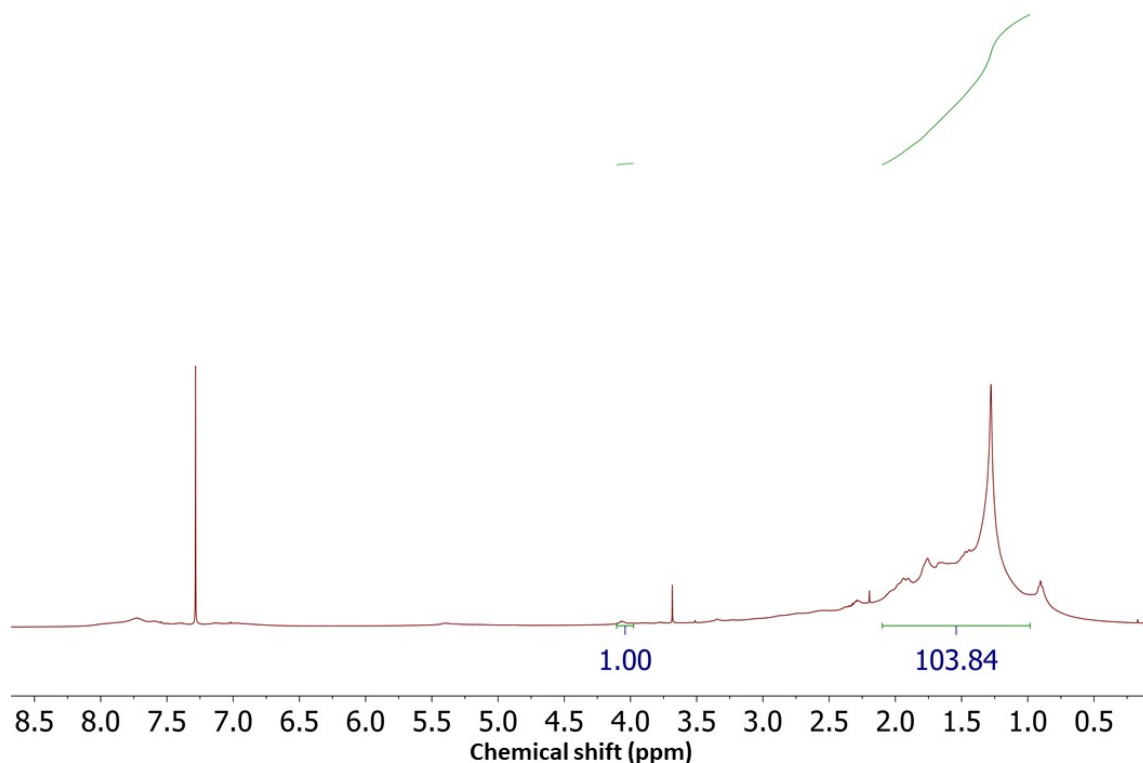
Figure S4. *^{1}H-NMR spectrum of polymer product with 98% dechlorination (CDCl$_3$, 400 MHz). (reaction conditions: 1.5 mmol PVC, 0.2 mmol ZnCl$_2$, 0.01 mmol HCl(CO)Ru(PPh$_3$)$_3$ in 2 mL methyl cyclohexanecarboxylate, reaction for 16h at 180°C under 20 bar H$_2$).*

3. 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 100% transmission. Firstly, as illustrated in **figure S5.**, different polymers with variable content of Cl were characterized by the vibrational peaks. PVC displays more intense Cl-related vibrational peaks (**spectrum A**), while chlorinated polyethylene (CPE with 25 m% Cl, **spectrum B**) and PE (**spectrum C**) display predominantly intense peaks for -CH$_2$-related vibrations. The assigned peaks for each polymer are:

PVC (in cm^{-1}): 2993 (w, ν_s CHCl), 2950 (w, ν_{as}CH$_2$) , 2843 (w, ν_sCH$_2$), 1425 (s, δCH$_2$), 1329 (w), 1252 (s, δCHCl), 1077 (s, C-C stretch), 969 (s, CH$_2$-rocking), 861 (w) , 829 (w), 691 (m, C-Cl stretch), 608 (s, C-Cl stretch).

CPE (in cm^{-1}): 2911 (s, ν_{as}CH$_2$), 2845 (s, ν_sCH$_2$), 1425 (s, δCH$_2$), 1252 (m, δCHCl), 1077 (m, C-C stretch), 718 (s, CH$_2$-rocking).

PE (in cm^{-1}): 2913 (s, ν_{as}CH$_2$), 2846 (s, ν_sCH$_2$), 1461 (s, δ_{as}CH$_2$), 718 (s, CH$_2$-rocking).

These peaks were used as references to identify reaction products, since the reaction products display various degrees of dehydrochlorination-hydrogenation.[1]
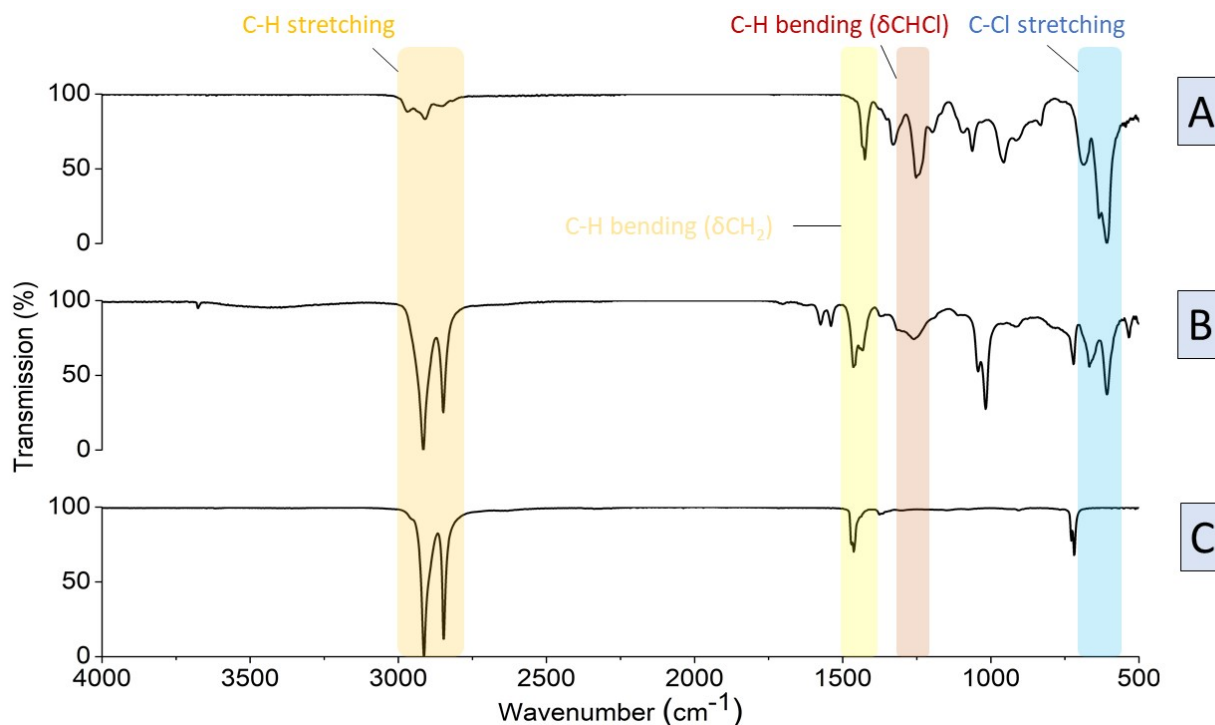
Figure S5. *ATR FTIR of virgin polymers; with (A) PVC, (B) chlorinated PE with 25 m% of Cl and (C) PE. Boxes indicate characteristic vibrational peaks for the three polymers, with varying chloride content.*

4. Solvent screening for tandem reaction of virgin PVC
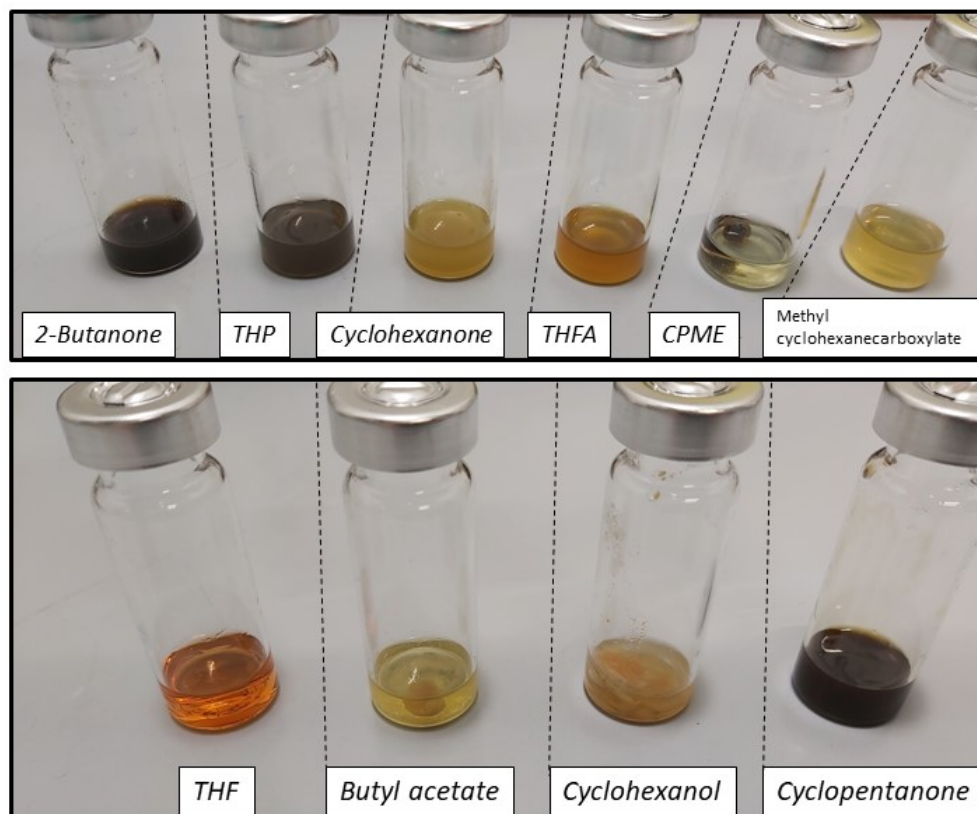
Figure S6. *Reaction mixtures obtained after solvent screening for tandem reactions. (Conditions: 1.5 mmol of virgin HMW-PVC, 0.2 mmol ZnCl$_2$, 0.01 mmol HCl(CO)Ru(PPh$_3$)$_3$, 2 mL solvent, 180°C under 20 bar H$_2$ for 16 h).*
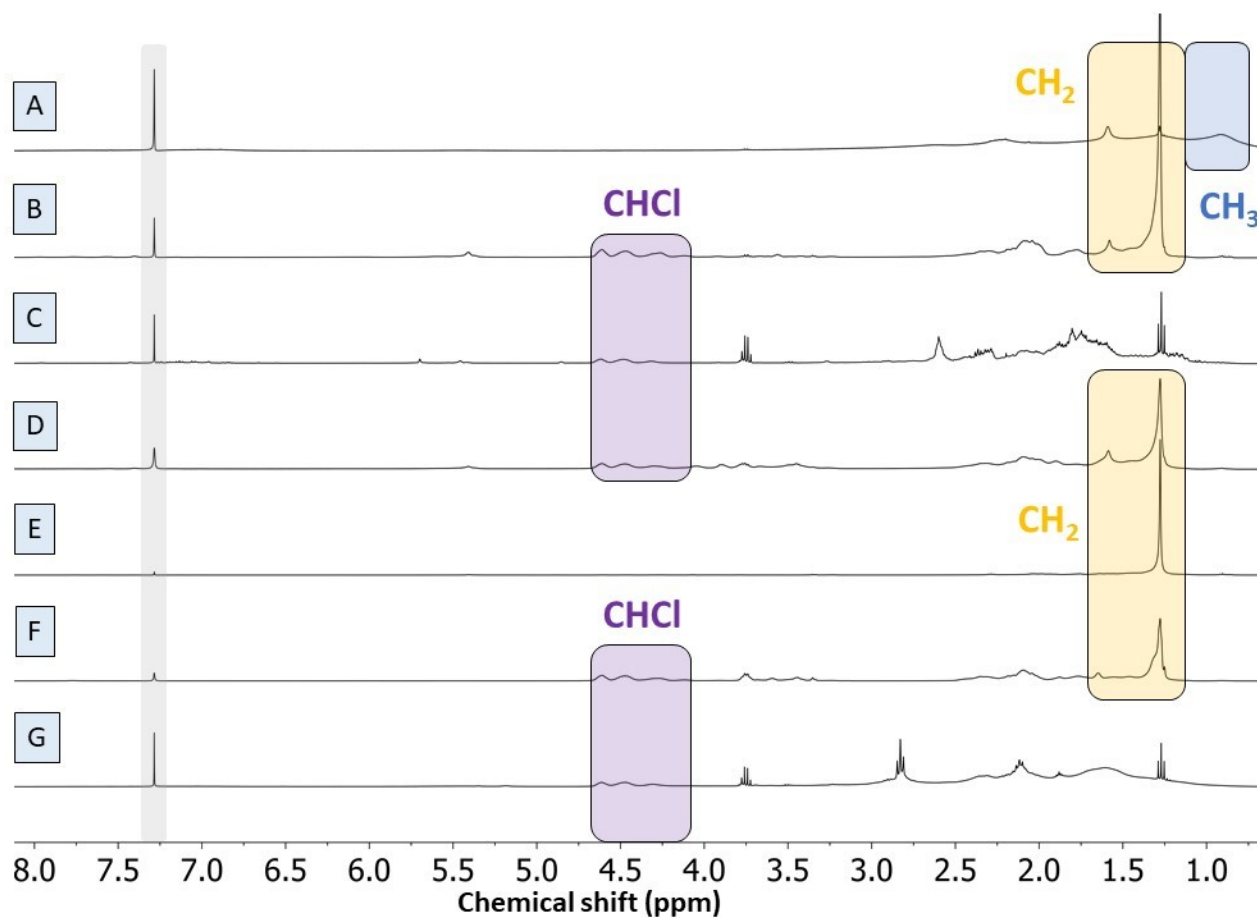
Figure S7. ^{1}H-NMR spectra (CDCl$_3$, 400 MHz) of polymer products that were obtained after tandem reactions in different solvents. Product from (A) 2-butanone, with high CH$_3$/CH$_2$-group ratio and full dechlorination (B) THP, with 63% dechlorination (C) cyclohexanone, contains aldol condensation impurities (D) THFA, with 45% dechlorination (E) methyl cyclohexanecarboxylate, with 100% dechlorination (F) THF, with 50% dechlorination (G) cyclopentanone, contains aldol condensation impurities. (Conditions: 1.5 mmol of virgin HMW-PVC, 0.2 mmol ZnCl$_2$, 0.01 mmol HCl(CO)Ru(PPh$_3$)$_3$, 2 mL solvent, 180°C under 20 bar H$_2$ for 16h).
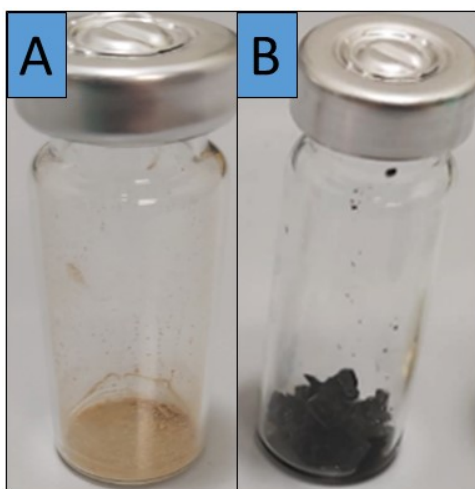
Figure S8. *Pictures of polymer products from tandem reactions of HMW-PVC (conditions with 1.5 mmol HMW-PVC, 0.2 mmol ZnCl$_2$ in methyl cyclohexanecarboxylate solvent at 180°C under 20 bar H$_2$). Different solvent volumes led to different products: A) Using 2 mL solvent, efficient dehydrochlorination-hydrogenation gave white-yellow powder. B) using 1 mL solvent, charring due to limited hydrogenation led to blackening of the product.*

**5. Investigated molecular weight values in array of (virgin) PVC samples**
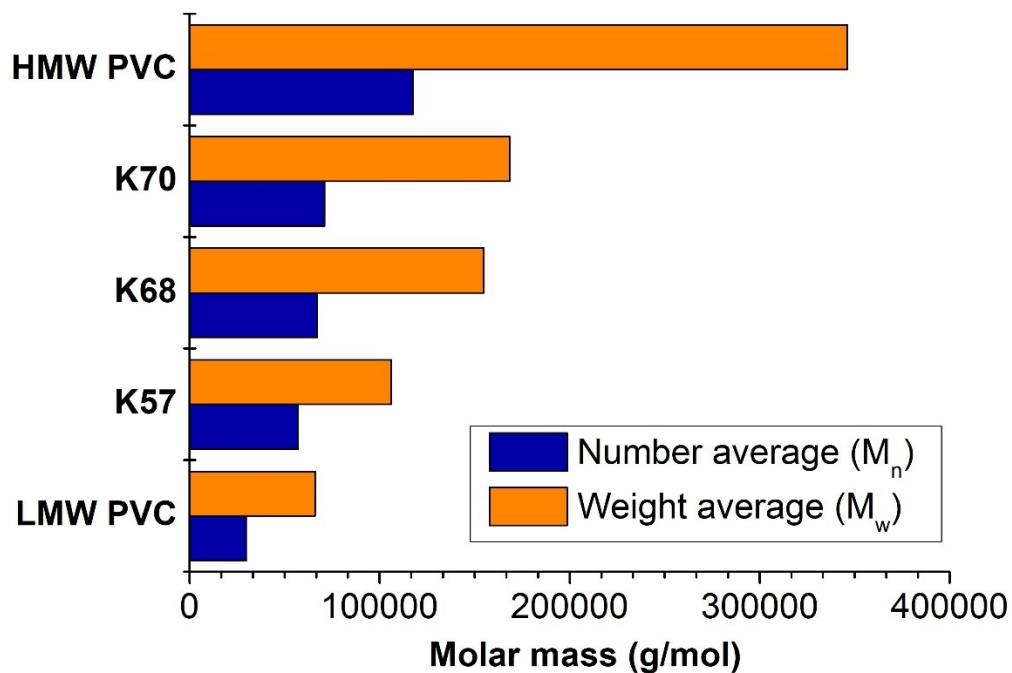
Figure S9. *Relation between rheology-based Fikentscher K-values and the determined Molar mass averages (M_n and M_w) of PVC samples by GPC. GPC measurements were calibrated using polystyrene standards in THF, with detection by refractive index (RI).*

5. Post-consumer waste sample composition

5.1 Source of investigated waste applications

Samples of various types of crude stabilized PVC were collected from municipal waste collection, and these samples were grinded to powders (**Figure S10**), on which no subsequent purification was performed. The samples originate from applications such as PVC pipes, cables, films and shoe soles. ATR-FTIR analysis showed the sample powders from construction to be of homogeneous composition. The PVC shoe sole was of heterogeneous nature, containing approximately 90% PVC which was seen by ATR-FTIR spectra being slightly different depending on the measuring position on the sample material.
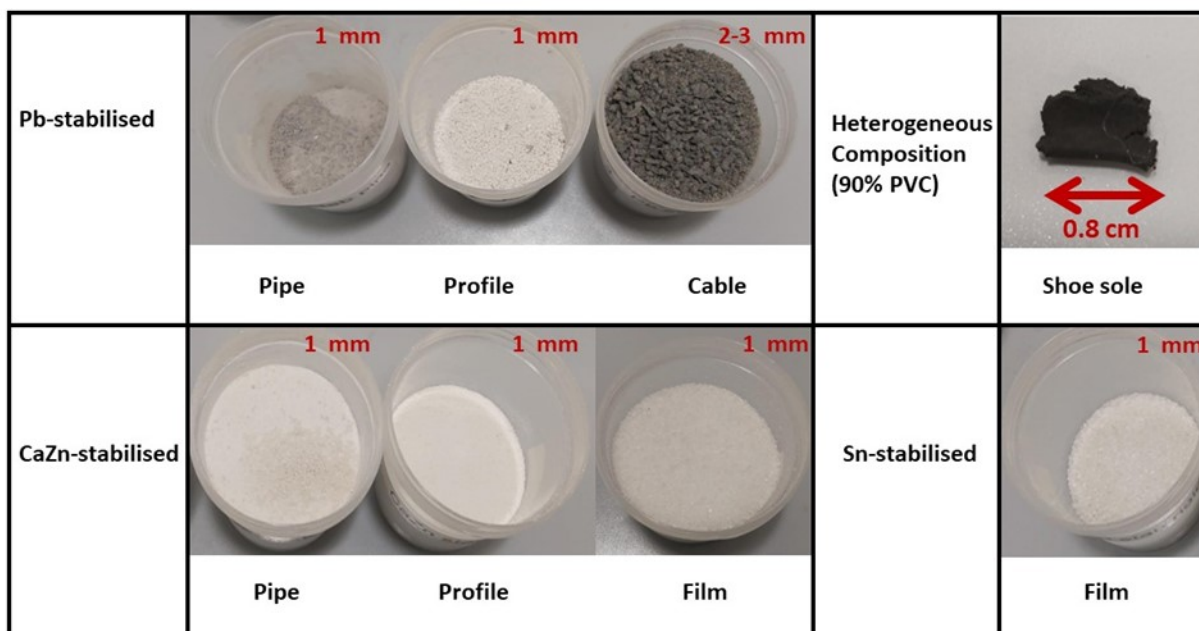
Figure S10. *Pictures of the investigated ground powder samples and the shoe sole that consist of PVC and additives, originating from waste applications. Lengths indicated in red illustrate the mean particle size of the waste material.*

Various post-consumer waste PVC samples were investigated on their additive content. By thermogravimetric analysis (TGA), the inorganic filler and metal content were determined. Additionally, the post-consumer waste samples were analyzed by liquid ^{1}H-NMR (d^{8}-THF, 400 MHz) for their organic additive content such as plasticizers.

5.2 Thermogravimetric analysis (TGA)

When comparing TGA measurements of the various waste applications from the construction sector, with virgin PVC (**Figure S11**), significant differences in non-degradable content were observed. Additionally, the thermal degradation of a PVC-containing shoe sole was investigated (**Figure S12**).

Firstly, after thermal degradation under N_2-atmosphere at temperatures up to 700°C, virgin PVC retained only 8% of its original mass. It has been previously found that a first mass loss stage at 280°C is caused by HCl release from the polymer, while subsequent degradation is related to scission reactions of the polymer chain with charring leading to the non-degradable content of virgin PVC. For the PVC waste applications, different contents of this non-degradable residual mass after the heating procedure, can be attributed to the inorganic content of the polymer. Therefore, the inorganic filler content of the investigated waste PVC materials was calculated by subtracting 8% (as would be observed for pure PVC) from the residual mass after the heating procedure.
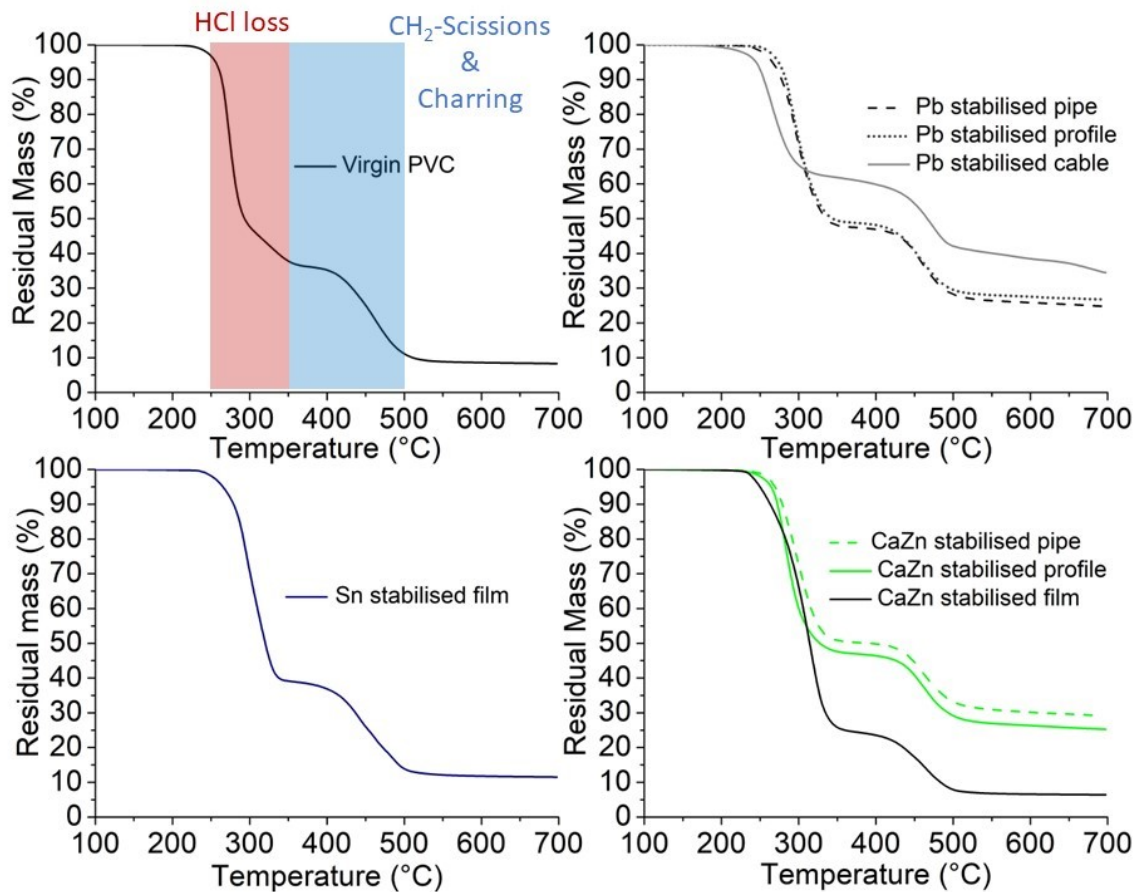
Figure S11. *Thermogravimetric analysis (TGA) of virgin PVC and ground waste materials from construction. Measurements with heating rate of 10°C/min under N_2-atmosphere. The thermal degradation stages are marked for virgin PVC.*
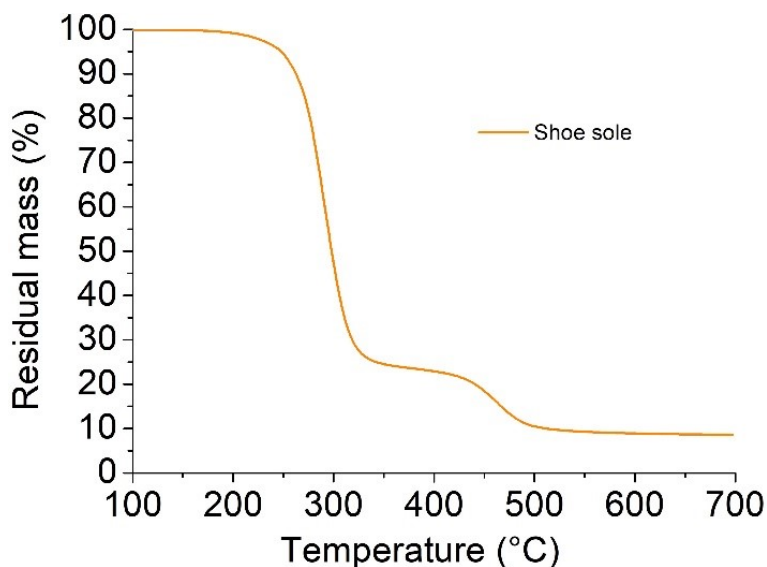
Figure S12. *Thermogravimetric analysis (TGA) of a shoe sole material, containing PVC. Measurement with heating rate of 10°C/min under N_2-atmosphere.*

The measured residual mass using TGA and the derived inorganic content (m%) of the waste applications are listed in **Table S2**.

Entry	Waste application	Residual mass after heating (%)	Inorganic content (%)
1	Virgin PVC	8	0
2	Pb-stabilised pipe	25 (± 1.1)	17 (± 1.1)
3	Pb-stabilised profile	27 (± 0.8)	19 (± 0.8)
4	Pb-stabilised cable	34 (± 1.6)	26 (± 1.6)
5	Sn-stabilised rigid film	12 (± 0.2)	4 (± 0.2)
6	CaZn-stabilised pipe	29 (± 0.6)	21 (± 0.6)
7	CaZn-stabilised profile	25 (± 0.3)	17 (± 0.3)
8	CaZn-stabilised film	6 (± 0.2)	0 (± 0.2)
9	Shoe sole	9 (± 0.2)	1 (± 0.2)

Table S2. *Residual mass and the derived inorganic filler content of PVC waste materials after thermogravimetric analysis to 700°C (under N_2 atmosphere with 10°C/min heating rate). Average values are given (± standard deviation) from triplicate measurements on different samples of the ground waste powders.*

6. Gel Permeation Chromatography (GPC) for molecular weight determination

GPC measurements were done on an Agilent 1260 Infinity II GPC device using a PL 1110-6500 column with THF as the mobile phase. The column was kept at 35°C for measurements. Signals were monitored using a refractive Index Detector (RID), for which the Molar Weight (MW) averages of polymers were determined according to Polystyrene standards. Column calibration was done by measuring a set of MW in the range of 162-364000 g/mol (**Table S3**).

Column Calibration Data Points

Point	Peak Max RT (mins)	MW	Log MW	Point in Use?	Percent Error
1	6,34320	364000	5,56	Yes	0,39
2	6,58800	200500	5,30	Yes	-1,22
3	6,93360	89050	4,95	Yes	-0,45
4	7,19280	49350	4,69	Yes	1,95
5	7,42320	28440	4,45	Yes	1,46
6	7,74000	13440	4,13	Yes	1,60
7	8,06400	6250	3,80	Yes	1,83
8	8,31600	3320	3,52	Yes	-1,69
9	8,76960	1180	3,07	Yes	2,37
10	8,84880	935	2,97	Yes	-2,12
11	9,17280	370	2,57	Yes	-19,72
12	9,65520	162	2,21	Yes	12,86

Table S3. *Calibration curve set-up of polystyrene standards in THF with RI detector, with relation retention time (RT)-MW, for determination of MW of the polymers.*

7. Activity of the ZnCl$_2$-catalyst

The dehydrochlorination activity was investigated by using only one of the catalysts for PVC conversion. Using only ZnCl$_2$ for reaction conditions at 180°C, resulted in a color change in the initial minutes of reaction, from transparent yellow to black with precipitation of solids after 7 min (**figure S13**). UV-Vis spectroscopy of the reaction mixture in this timeframe, showed increasing absorbance at 254 nm, and higher wavelengths, which indicates aromatics formation and increased lengths of polyene sequences, respectively.
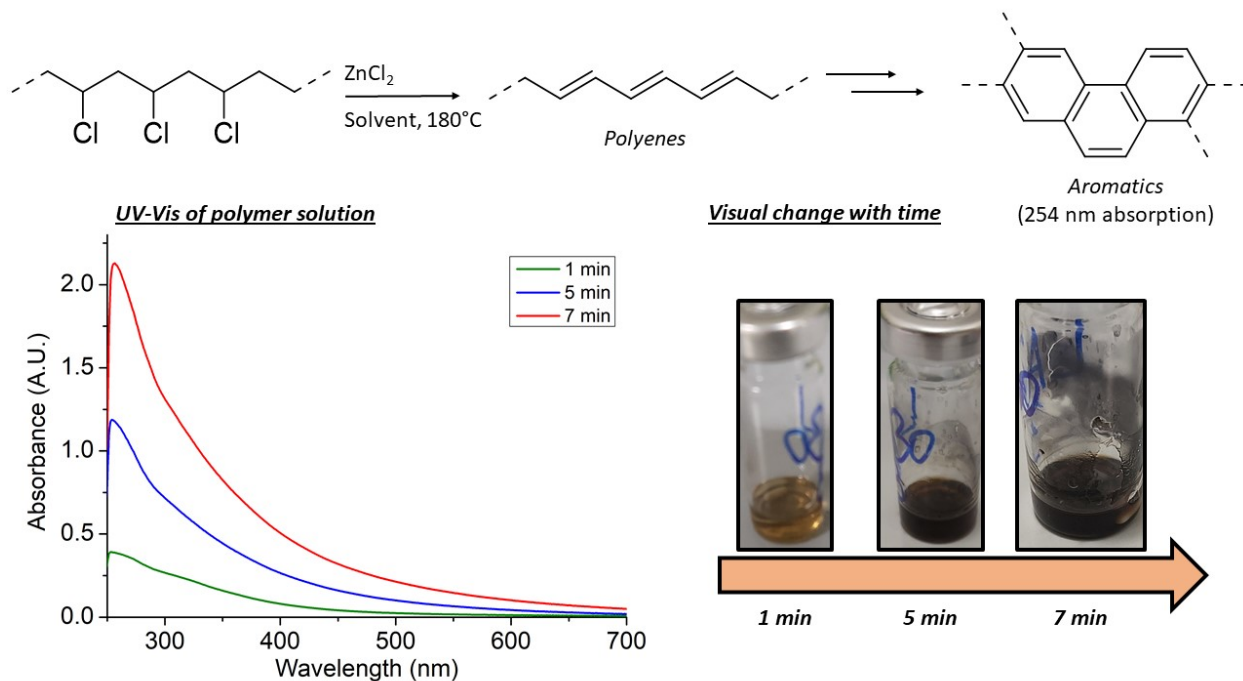

Figure S13. *Visual change of the reaction mixture in the initial minutes of dehydrochlorination using only ZnCl$_2$, and UV-Vis absorbance spectra of the mixture (conditions: 1.5 mmol LMW-PVC, 0.2 mmol ZnCl$_2$, 1 mL methyl cyclohexane carboxylate, with heating at 180°C).*

8. Polymer products from studying the dual catalyst activity

Further elucidation of the polymer products, after varying the employed catalysts, was done by liquid ^{1}H- and ^{13}C-NMR (CDCl$_3$, 400 MHz). Analysis of the ^{1}H-NMR spectra (**Figure S14**), showed more structurally diverse products than the initial PVC when using the Ru catalyst for the tandem reaction. Using the Ru catalyst, incomplete dechlorination of PVC is achieved but the products contain =CH-moieties (from double bonds, δ 5.4 ppm), residual CHCl-groups (δ 4.6-4.0 ppm), with adjacent α-CH$_2$-groups (δ 2.5-2.0 ppm). Allylic CH$_2$ gives rise to a peak at δ2.0 ppm and the CH$_2$-groups in ethylene-ethylene sequences lead to peaks at δ 1.6-1.3 ppm. Fully reacted products, as obtained when combining ZnCl$_2$ and the Ru-catalyst, gave rise to CH$_2$-group peaks (δ 1.6-1.3 ppm) and peaks of CH$_3$-groups (δ 0.9 ppm).
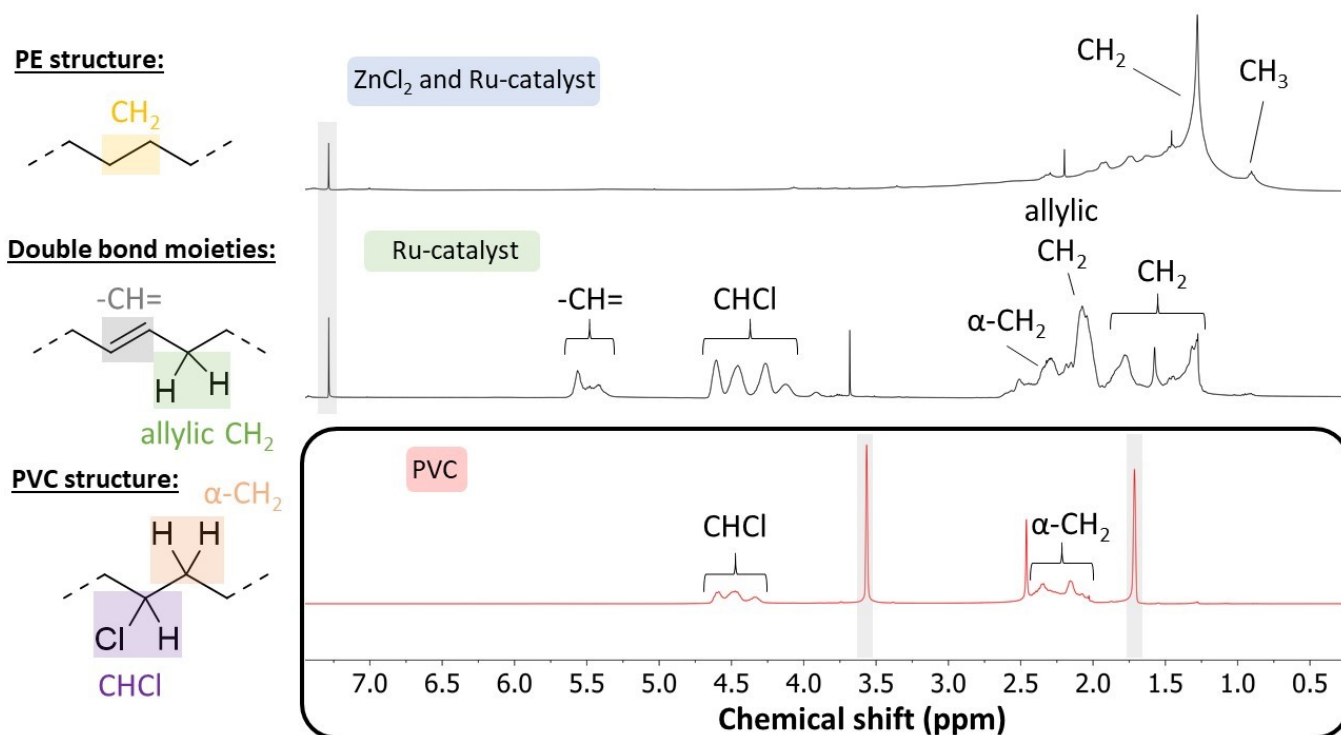
Figure S14. *^{1}H-NMR spectra and structural assignments of PVC (d[8]-THF, 400 MHz) and polymer products after applying tandem-dehydrochlorination hydrogenation conditions, using both catalysts or only Ru-catalyst (CDCl$_3$, 400 MHz). Greyed peaks at 7.26 ppm originate from CHCl$_3$ and peaks at 3.57 ppm and 1.77 ppm originate from THF. (Conditions: 0.2 mmol ZnCl$_2$ and/or 0.01 mmol HCl(CO)Ru(PPh$_3$)$_3$ per 1.5 mmol LMW-PVC, reaction in 2 mL methyl cyclohexane carboxylate at 180°C under 20 bar H$_2$, for 16h.)*

Analysis of the fully reacted products by ^{13}C-NMR (**Figure S15**), using $ZnCl_2$ and the Ru-catalyst, demonstrates a complete disappearance of the CHCl shifts (δ 63-56 ppm) of PVC to a polymer with distinct CH_2-groups (28 ppm), for which almost no branches were formed, except for a low intense peak of CH_3-groups. On the other hand, employing only Ru-catalyst led to a partially converted product that contained some CH_2-groups (28 ppm), and CH_2-groups on the allylic position beside the residual double bonds (37 ppm). The incomplete dechlorination by using only Ru is apparent by residual peaks of CHCl and their adjacent α-CH_2 groups.
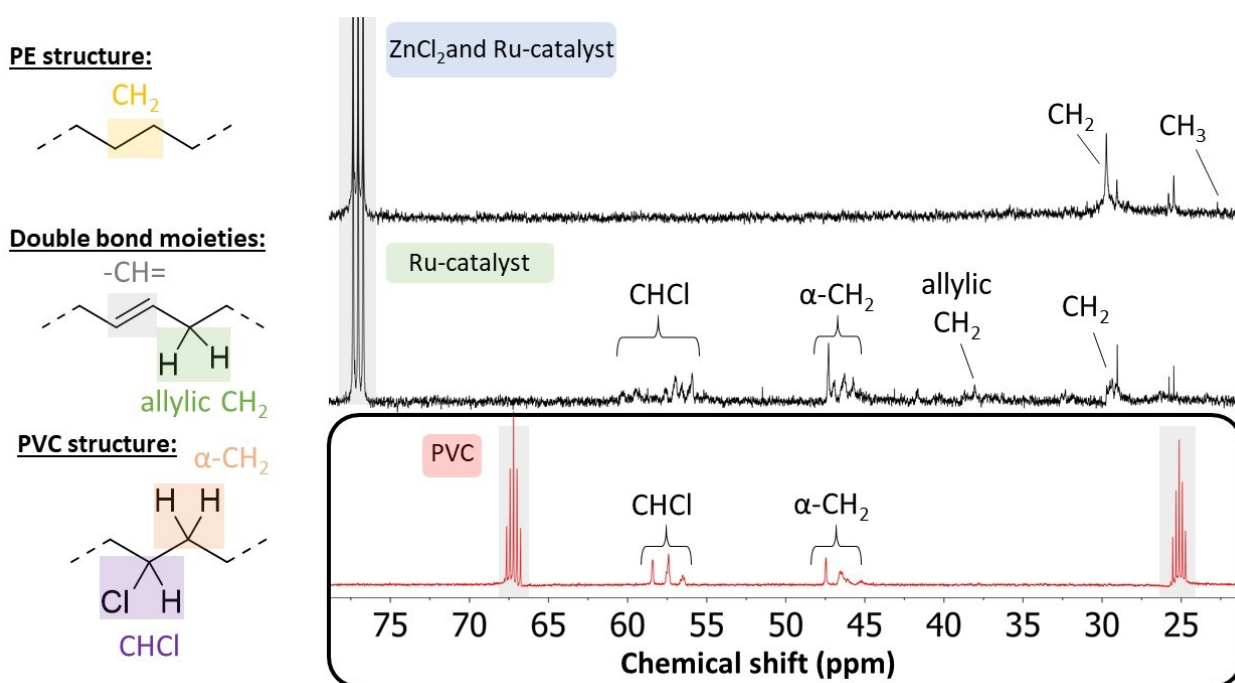
Figure S15. *^{13}C-NMR spectra of PVC (d^8-THF, 400 MHz) and polymer products after PVC conversion using both catalysts or only Ru-catalyst (general conditions with 1.5 mmol LMW-PVC, 0.2 mmol ZnCl$_2$, 0.01 mmol HCl(CO)Ru(PPh$_3$)$_3$, 1 ml methyl cyclohexanecarboxylate at 180°C under 20 bar H$_2$). Grey boxes indicate peaks of THF (3.57 and 1.77 ppm) and CHCl$_3$ (7.26 ppm). (Conditions: 0.2 mmol ZnCl$_2$ and/or 0.01 mmol HCl(CO)Ru(PPh$_3$)$_3$ per 1.5 mmol LMW-PVC, reaction in 2 mL methyl cyclohexanecarboxylate at 180°C under 20 bar H$_2$, for 16h.)*

9. X-Ray absorption spectroscopy (XAS)

The conditions of the acquired samples for XAS analysis are listed in **Table S4**.

Processing of experimental XAS data, including averaging over eight scans, energy calibration, normalization, extraction of $\chi(k)$ signals and Fourier analysis of EXAFS, were performed in the Athena and Artemis programs of the Demeter package.[2] The fitting was done in R-space in the $1.3 - 2.9$ Å range simultaneously on k^1-, k^2-and k^3-weighted data, applying the Hanning window from 3 to 11.5 Å^{-1}. The theoretical phases and amplitudes were calculated by FEFF6.[3] Six scattering paths were used in the fit for the sample with only Ru-catalyst (after 16h reaction) or fresh Ru-catalyst, and seven paths for the sample with both ZnCl$_2$ and Ru-catalyst (after 16h reaction) (**Table S5**). Ru K-edge EXAFS oscillations in k-space (k^2-weighted) are illustrated in **Figure S16**.

Entry	Ru-precursor	ZnCl$_2$ added	PVC added	Sample type
1	HCl(CO)Ru(PPh$_3$)$_3$	/	/	pellet
2	HCl(CO)Ru(PPh$_3$)$_3$ (0.01 mmol)	/	1.5 mmol	in methyl cyclohexanecarboxylate solution (2 mL, after heating at 180°C under 20 bar H$_2$, for 16h)
3	HCl(CO)Ru(PPh$_3$)$_3$ (0.01 mmol)	0.2 mmol	1.5 mmol	in methyl cyclohexanecarboxylate solution (2 mL, after heating at 180°C under 20 bar H$_2$, for 16h)

Table S4. *Conditions for the investigated XAS samples.*

Scattering path	Ru-C	Ru-P	Ru-Cl	Ru-O	Ru-CO	Ru-COC	Ru-Ru
Fresh Ru-catalyst (Entry 1)							
N	1	3	1	1	2	1	–
R	1.84 ± 0.01	2.46 ± 0.12	2.29 ± 0.17	2.96 ± 0.04	2.96 ± 0.04	2.96 ± 0.04	–
σ^2	0.003	0.004 ± 0.005	0.001 ± 0.007	0.004 ± 0.008	0.004 ± 0.008	0.004 ± 0.008	–
ΔE_0	-5.68 ± 8.04						
R-factor	0.013						
Ru-catalyst without ZnCl$_2$ (Entry 2)							
N	1.3	1.32 ± 1.74	2.4	2	4	2	–
R	1.83 ± 0.02	2.29 ± 0.04	2.41 ± 0.04	2.92 ± 0.08	2.92 ± 0.08	2.92 ± 0.08	–
σ^2	0.003	0.002 ± 0.003	0.002 ± 0.003	0.003 ± 0.004	0.003 ± 0.004	0.003 ± 0.004	–
ΔE_0	-10.2 ± 9.51						
R-factor	0.006						
Ru-catalyst with ZnCl$_2$ (Entry 3)							
N	1.1	1.8	1	1.4	2.8	1.4	0.5
R	1.71 ± 0.13	2.35 ± 0.02	2.31 ± 0.13	3.05 ± 0.05	3.05 ± 0.05	3.05 ± 0.05	2.57 ± 0.13
σ^2	0.003	0.002 ± 0.003	0.002 ± 0.003	0.001 ± 0.008	0.001 ± 0.008	0.001 ± 0.008	0.002 ± 0.003
ΔE_0	-8.95 ± 7.84						
R-factor	0.022						

Table S5. *Structural parameters obtained from the EXAFS data analysis, where N is the average coordination number, R – the Ru-X distance, σ^2 – Debay-Waller factor, ΔE_0 – energy shift. The S_0^2 factor was fixed to the value 1 obtained by fitting the EXAFS spectrum of Ru foil with N = 12.*
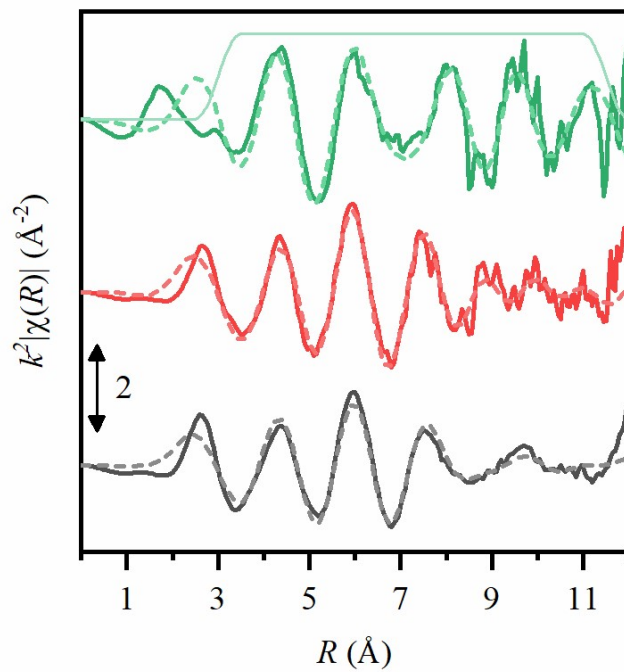
Figure S16. *Ru K-edge EXAFS oscillations in k-space (k^2-weighted) of fresh Ru-catalyst (gray, entry 1), Ru-catalyst without $ZnCl_2$ (red, entry 2), Ru-catalyst with $ZnCl_2$ (green, entry 3).*

10. Characteristics of the converted PVC products

When comparing the molecular weight distribution of the products obtained from tandem dehydrochlorination-hydrogenation reactions with that of virgin polymers, some differences are observable (**Table S6**). Firstly, the polymer product with low M_n and M_w, formed when using $ZnCl_2$-Ru (**Entry 3**) has a slightly lower polydispersity index (PDI) than the virgin PVC starting material (**Entry 4**). This may be related to chain splitting reactions, which decrease the dispersity of the product. Secondly, the polymer from using $ZnCl_2$-Ru (**Entry 3**) has a molecular weight that is similar to that of virgin LDPE material which has a very low molecular weight (**Entry 2**). Finally, an incompletely converted product obtained by using only Ru, without $ZnCl_2$ (**Entry 4**) has an increased PDI compared to virgin PVC, which can originate from cross linking reactions. Hence, the molecular weight distribution is broadened by crosslinking, and narrowed by the chain splitting reactions.

Entry	Polymer	M_n (g/mol)	M_w (g/mol)	Degree of dechlorination (%)	PDI
1	LMW-PVC (virgin polymer)	29799	66005	Not applicable	2.2
2	LMW-LDPE (virgin polymer)	1781	3624	Not applicable	2.0
3	Polymer product (using $ZnCl_2$-Ru)	1798	3500	100	1.9
4	Polymer product (Using only Ru)	29800	75719	64	2.5

Table S6. *Molecular weight characteristics of polymer products and comparison with low molecular weight (LMW)-virgin PVC and PE. The number average (M_n) and weight average (M_w) molecular masses and polydispersity index (PDI) are displayed for products. (Conditions: 1.5 mmol PVC, 0.01 mmol Ru-catalyst, 0.2 mmol $ZnCl_2$, 2 mL methyl cyclohexanecarboxylate, 20 bar H_2, 16h at 180°C)*

The thermal stability of the polymer products was compared with that of virgin LDPE by TGA (10 °C/min heating rate under N_2-atmosphere). The thermal degradation profile of the polymer product that was obtained by using only Ru-catalyst (64% dechlorination, **Figure S17, A**), has two distinct mass loss stages which originate from residual HCl release followed by chain scissions in the second stage. The product with complete dechlorination, which was obtained using $ZnCl_2$-Ru (100% dechlorination, **Figure S17, C**) had only a single mass loss stage, at comparable temperature as virgin PE (**Figure S17, blue box**). The related differential thermal gravimetry (DTG) of the incompletely dechlorinated product (**Figure S17, B**) shows that the two mass loss stages occur mostly at 280°C (HCl-release) and 460°C (chain scissions). The product with complete dechlorination (**Figure S17, D**) solely displays a large mass change at 460°C (chain scission). Hence, full dechlorination of polymer products leads to similar thermal properties as found in virgin PE material.

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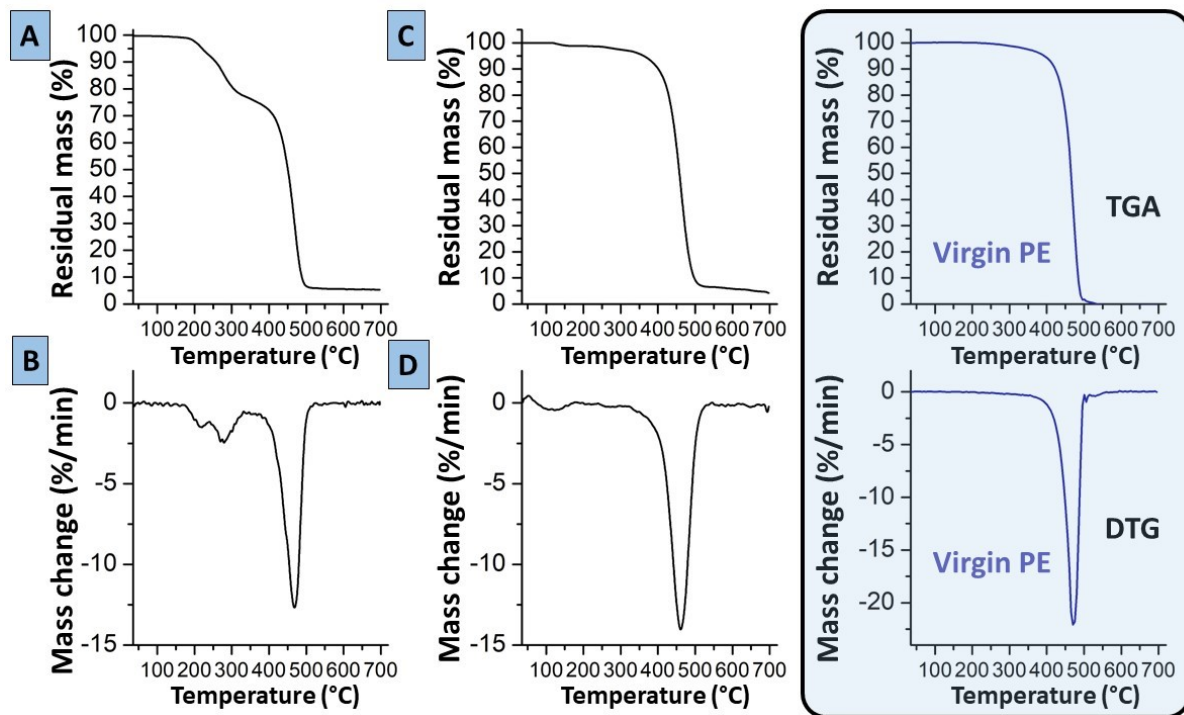
Figure S17. *Thermogravimetric analysis (TGA) measurements and differential thermogravimetry (DTG) of polymer products obtained from tandem dehydrochlorination-hydrogenation of PVC (Conditions: 1.5 mmol PVC, 0.01 mmol Ru-catalyst, 0.2 mmol ZnCl$_2$, 2 mL methyl cyclohexanecarboxylate, 20 bar H$_2$, 16h at 180°C). With the TGA (A) and DTG (B) of a polymer product with 100% dechlorination, using ZnCl$_2$-Ru; and the TGA (C) and DTG (D) of a polymer product with 64% dechlorination, using only Ru-catalyst. Marked TGA and DTG curves in blue box are measurements of virgin LMW-PE, as a reference.*

11. Reusability of the catalysts and the solvent

The recyclability of the catalysts was evaluated by a solvent recuperation experiment (**Figure S17**). For this, the reaction was initially performed with 0.2 mmol $ZnCl_2$, 0.01 mmol $HCl(CO)Ru(PPh_3)_3$ and 2 mL of methyl cyclohexanecarboxylate solvent for the conversion of 1.5 mmol LMW-PVC. After the 1st and subsequent reaction cycles, the polymer product was precipitated by adding 4 mL of methanol to the reaction mixture. Thereafter the product was isolated by centrifugation and decantation to remove the solvent. The methyl cyclohexanecarboxylate solvent was then again purified, by heating it at 80°C overnight to evaporate the methanol. The subsequent reaction cycle was then repeated by adding fresh virgin PVC (1.5 mmol) for the next conversion reaction in the purified solvent. The mass of recovered reaction products (PE-like product or char) was determined gravimetrically.

Two types of solvent recovery experiments were performed. In the first type of experiments the solvent was recovered and reused without adding new Ru-catalyst for the subsequent reaction (**Figure S18, top**). In the second type of experiments, new $HCl(CO)Ru(PPh_3)_3$-catalyst (0.01 mmol) was added before each reaction (**Figure S18, middle**). Additionally, after every reaction cycle, the mass fraction of recovered solvent was determined gravimetrically (**Figure S18, bottom**).

When reactions were performed without renewing the Ru-catalyst, charred reaction products were obtained after the 2nd and 3rd reaction cycle, indicating that the $ZnCl_2$ catalyst retained its dehydrochlorination activity after every cycle. The Ru catalyst was found to have lost its hydrogenation activity after the 2nd cycle. This may be due to HCl accumulation in the reaction solvent during multiple cycles, which leads to Ru catalyst deactivation. When renewing the Ru catalyst, PE-like reaction products were obtained after every cycle, with 100% dechlorination compared to PVC. Additionally, when comparing the recovered solvent fractions, there was a notable loss of solvent when no new Ru-catalyst was added between cycles. The chars formed under these conditions, were swollen gels with a mass of >100% of the original, thereby indicating that the solvent was lost because of incorporation in the charred polymer products.
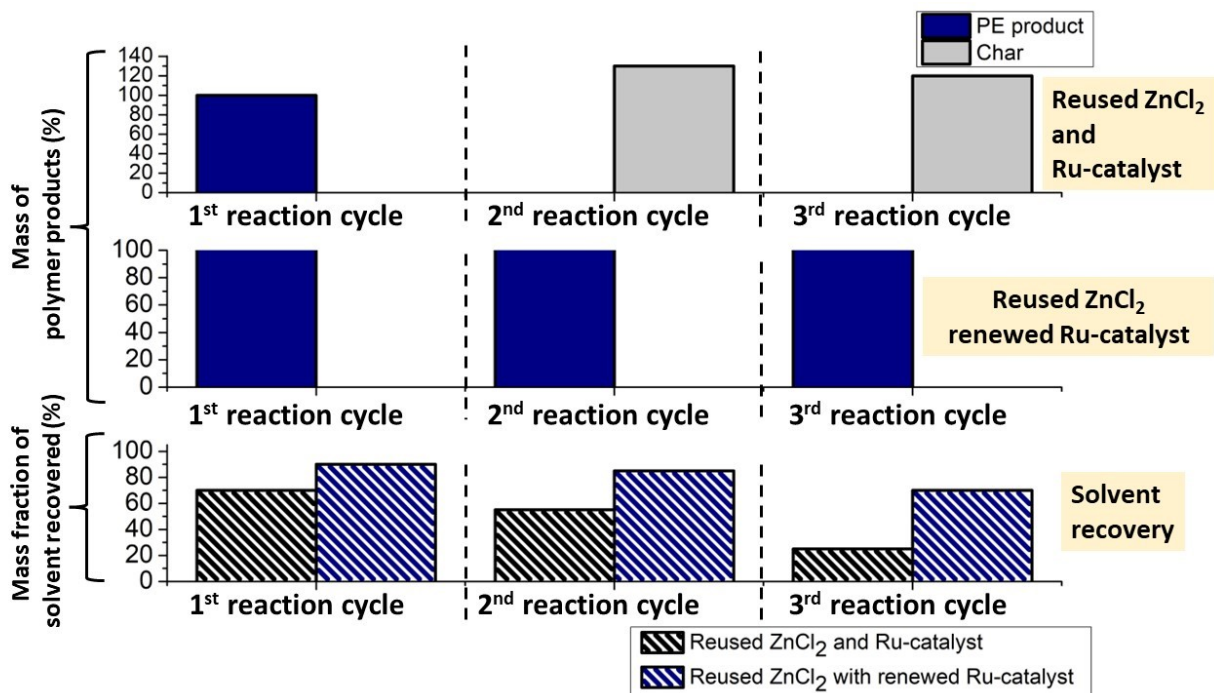
Figure S18. *Recycling experiment of the catalysts (ZnCl$_2$ and the Ru-complex) and the methyl cyclohexanecarboxylate solvent during three reaction cycles. (Conditions per reaction cycle: 1.5 mmol PVC, 0.01 mmol Ru-catalyst, 0.2 mmol ZnCl$_2$, 2 mL methyl cyclohexanecarboxylate, 20 bar H$_2$, 16 h at 180°C). After each reaction, solvent was recovered and reused for the next cycle. When reusing the solvent, without adding new Ru-catalyst, char was obtained in 2-3rd cycles (top). When reusing the solvent and adding new fresh Ru-catalyst for 2-3rd cycle, PE-like product was obtained after every cycle (middle). Recovered solvent fraction after each cycle when Ru-catalyst is reused or renewed (bottom).*

10. References

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