

Electronic Supplementary information

Chemical Upcycling of Polybutadiene into Size Controllable α,ω -Dienes and Diesters via Sequential Hydrogenation and Cross-Metathesis

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References

Experimental

1. Materials

High molecular weight cis-polybutadiene (PBD) with a molecular weight average (M_w) of 200,000-300,000 g/mol, ethyl vinyl ether, $\text{Ru}(\text{PPh}_3)_3\text{Cl}_2$, the n-alkane standard mix $\text{C}_7\text{-C}_{30}$ and the metathesis catalysts; (dichloro[1,3-bis(2,4,6-trimethylphenyl)-2-imidazolidinylidene](3-phenyl-1H-inden-1-ylidene)(tricyclohexylphosphine)ruthenium(II) as Grubbs Catalyst® M202, cis-[1,3-bis(2,4,6-trimethylphenyl)-2-imidazolidinylidene]dichloro(3-phenyl-1H-inden-1-ylidene)(triisopropylphosphite)ruthenium(II) as Grubbs Catalyst® M220) were acquired from Sigma-Aldrich. All employed solvents (cyclopentyl methyl ether (CPME), ethanol, tetrahydrofuran (THF), methanol and chloroform-d) were of technical grade without additional purification or drying. 1,4-Benzoquinone (BQ) and 1,9-decadiene were supplied by TCI Belgium. n-Nonane, 1,5-hexadiene, 5wt% palladium on Al_2O_3 and dimethyl maleate (DMM) were supplied by Acros. The 66wt% nickel on silica-alumina was supplied by Thermo Fisher Scientific. 5 wt% nickel on Al_2O_3 and 5wt% nickel on SiO_2 were prepared as described by Cuypers *et al.*¹ The rubber phase of a commercial HIPS sample was obtained as described by Giakoumakis *et al.*² Small scale reactions under pressurised gas atmosphere (H_2 or ethylene) were performed in 15 mL home-made autoclave reactors equipped with digital manometers, that can withstand pressures up to 60 bar. The pressure was monitored using an IFM PT 5423 pressure transmitter mounted on the reactor with a measuring range of 0-60 bar in combination with a Dixell xt controller display. Large scale hydrogenation was performed in a 600 mL Parr reactor. Large scale ethenolysis was performed in a 60 mL Premex reactor.

2. Reaction conditions

2.1 Hydrogenation

For the small scale hydrogenation, a stock solution of 1 M PBD (based on a butadiene repeat unit of 54 g/mol) was prepared in a vial by dissolving PBD (16 mmol, 864 mg PBD) in THF (15 mL) to a total volume of 16 mL at 50°C. Before reaction, the described quantity of $\text{Ru}(\text{PPh}_3)_3\text{Cl}_2$ catalyst or heterogeneous catalyst and 2 mL of the PBD stock solution (2 mmol PBD, 1 M, 2 mL) were brought into a liner. The liner was inserted into an autoclave reactor which was then sealed. After flushing with N_2 , the autoclave was brought under the investigated H_2 pressure. For homogeneous hydrogenation reactions under high pressure (30 bar H_2) and at low temperature (40°C), 2.4 mg of $\text{Ru}(\text{PPh}_3)_3\text{Cl}_2$ (0.0025 mmol, 0.125 mol% vs PBD unit) was used. For reactions under low pressure (8 bar H_2) at high temperature (80°C), 4.8 mg $\text{Ru}(\text{PPh}_3)_3\text{Cl}_2$ (0.005 mmol, 0.25 mol% per PBD unit) was used. The reaction mixture was then heated and magnetically stirred until a given pressure was reached. Thereafter, the autoclave was cooled in an ice-bath and THF (2 mL) was added to the reaction mixture. Subsequently, the reaction mixture was added to an excess of ethanol (~6 mL) as anti-solvent to precipitate the partially hydrogenated PBD. This polymer product was then isolated by decantation of the solvent excess whereafter it was dried under reduced pressure.

For the large scale hydrogenation in a 600 mL Parr reactor, a stock solution of 1.2 M PBD (based on a butadiene repeat unit of 54 g/mol) was prepared in a volumetric flask of 250 mL by dissolving PBD (300 mmol, 16.2 g PBD) in CPME (232 mL) to a total volume of 250 mL at 50°C. The mixture was brought in the glass liner of the Parr reactor together with 360 mg of $\text{Ru}(\text{PPh}_3)_3\text{Cl}_2$ (0.375 mmol, 0.125 mol% vs the butadiene unit). The reactor was closed and the 350 mL headspace was flushed with N_2 and loaded with 14.5 bar H_2 . The reactor was heated to 100°C and stirred at 500 rpm for 5h. The partially hydrogenated PBD was precipitated in 500 mL of MeOH as anti-solvent, spread out on a crystallization dish and dried overnight in a vacuum oven at 80°C.

The hydrogenation of the HIPS rubber phase (37.5 wt% PBD)² was performed in the home-made 15 mL autoclave. 72 mg (0.5 mmol C=C) was finely dispersed in 2 mL THF at 60°C. 4.8 mg $\text{Ru}(\text{PPh}_3)_3\text{Cl}_2$ (0.005 mmol, 1 mol% vs C=C) was brought in a glass liner together with the dispersion and placed in the autoclave. The reactor was sealed and the headspace was flushed with N_2 and afterwards charged to 12 bar H_2 . The autoclave was heated to 80°C for 2h. After the reaction, the product was precipitated in 5 mL of methanol, separated via decantation and dried under reduced pressure.

The polymer products were analysed by liquid ^1H NMR analysis (CDCl_3 , 400 MHz) at room temperature.

2.2 Metathesis reactions: Ethenolysis and Cross-metathesis

The ethenolysis of *trans*-5-decene (100 μmol , 18.9 μL , 1eq.) was performed in CPME (1 mL) with Grubbs Catalyst[®] M202 (0.01 eq., 0.95 mg) or Grubbs Catalyst[®] M220 (0.01 eq., 0.87 mg) for 1-4 hours. In some reactions, benzoquinone (0.185 eq., 2 mg) was added. Small scale ethenolysis of hPBD (100 μmol double bonds, 1 eq.) was performed in CDCl_3 (1 mL) with Grubbs Catalyst[®] M220 (0.01 eq., 0.87 mg) and benzoquinone (0.185 eq., 2 mg) for 1h. Large scale ethenolysis of hPBD (1.5 g, 12 mmol double bonds, 1 eq.) was performed in CDCl_3 (30 mL) in a 60 mL Premex reactor using Grubbs Catalyst[®] M202 (0.057 eq., 65 mg). After stirring the mixture overnight, undissolved particles were finely grounded using a mortar and pestle; this step is necessary to ensure complete dissolution during the large scale ethenolysis. Ethenolysis of partially hydrogenated rubber from HIPS (30 mg) was performed in CDCl_3 (1 mL) using 1 mg Grubbs Catalyst[®] M220 and 2 mg BQ for 1h at 100°C. Cross-metathesis of 1,5-hexadiene (0.5 mmol, 60 μL , 1eq.) and 1,9-decadiene (0.5 mmol, 92 μL , 1 eq.) with dimethyl maleate (DMM) (2.5 mmol, 313 μL , 5 eq.) as cross-coupling partner was performed in CDCl_3 (1 mL) with a reaction time of 4h using Grubbs Catalyst[®] M202 (0.01 eq., 4.75 mg) at 80°C. Cross-metathesis of the hPBD (100 μmol double bonds, 1 eq.) with dimethyl maleate (DMM) (0.5 mmol, 62 μL , 5 eq.) as cross-coupling partner was performed in CDCl_3 (1 mL) with a reaction time of 4h at 80°C using Grubbs M202 (0.01 eq., 0.95 mg). Solutions were brought in a glass liner loaded with benzoquinone and/or the catalyst. After sealing the reactor, the headspace was purged with N_2 and loaded with 8 bar C_2H_4 for all ethenolysis reactions. For the large scale reaction in the Premex reactor, the pressure was left to stabilize under magnetic stirring. The reactors were put in a preheated block and magnetically stirred at 400 rpm. After heating the reaction mixture for the designated reaction time, the reactors were cooled in a water bath. Subsequently, an aliquot (200 μL) of the reaction mixture was transferred to a vial for GC analysis. Additionally, *n*-nonane (100 μmol , 17.85 μL), as the external standard, and ethyl vinyl ether (25 μL), to quench the catalyst, were added prior to GC analysis.

2.3 One pot hydrogenation-ethenolysis

Hydrogenation of the PBD was performed under the high pressure, low temperature conditions described above, but with CDCl_3 as the solvent and a reaction time of 9h. After hydrogenation, 100 μL of the solution was mixed with 400 μL CDCl_3 for ^1H NMR analysis. For the ethenolysis reaction, 120 μL of the solution (100 μmol C=C, 1 eq.) was mixed with 880 μL of CDCl_3 and transferred to a liner with benzoquinone (0.185 eq., 2 mg) and Grubbs Catalyst[®] M220 (0.01 eq., 0.87 mg). The reactor was closed, purged with N_2 and loaded with 8 bar C_2H_4 . A reaction time of 1h at 100°C was used.

3. Methods

3.1 Calculation of hydrogen consumption

Measuring the headspace volume in the reactor

The home-made autoclave reactors with an empty volume of 15 mL were frequently tested for leaks at 60 bar H_2 using a flammable gas detector. H_2 and N_2 were assumed to behave like ideal gases.

The volume of the reactor with its internal components (i.e. with glass liner and stirring bar, but without the polymer solution) was measured according to the ideal gas law:

$$V = \frac{nRT}{P}$$

Here, n/P was obtained from m/P by weighing the reactor with its internal components at different pressures of N_2 , plotting the pressure versus the mass (see **Table S1** and **Figure S1**), calculating the slope (m/P) and using the molar mass of N_2 to finally calculate n/P .

Table S1. N_2 pressure in the reactor and gross weight of the pressurized reactor.

Pressure (bar)	Mass (g)
29.0	461.25
24.0	461.19
20.0	461.14
14.0	461.06
10.0	461.01
4.0	460.96
0.0	460.92

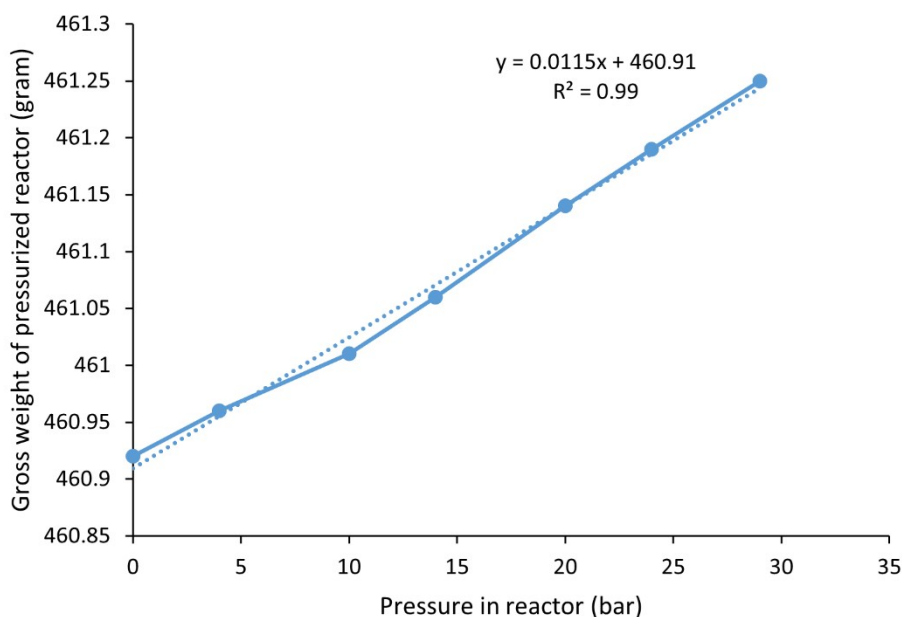


Figure S1. Plot of the N_2 pressure versus gross weight of the pressurized reactor.

From the N_2 pressure versus the weight of the reactor plot, the slope (m/P) was calculated to be 11.5 mg/bar. Using the molar weight of N_2 (28 mg/mmol), n/P is 0.411 mmol/bar or 0.411×10^{-8} mol/Pa.

With temperature T as 298K and the ideal gas constant R as $8.314 \frac{J}{mol \times K}$, the volume was calculated to be **10.2 mL**.

Estimation of hydrogen consumption during hydrogenations:

Upon volumetric addition of 2 mL of the 1M PBD solution (25 C=C/100C, 2 mmol C=C) to the reactor, the head space gas volume reduced to 8.2 mL. The reactor was then charged with the indicated H_2 -pressure (8 bar or 30 bar). To start the reaction, the reactor was placed in a heated block with magnetic stirring. After an initial pressure change in the first 5 minutes due to the heating of the reactor contents and dissolution of the H_2 , the pressure stabilized and this stabilized pressure was taken as the initial starting pressure.

According to the ideal gas law, it was calculated that **0.1 mmol H_2** in a volume of 8.2 mL at **40°C corresponds to 0.31 bar**, while at **80°C 0.1 mmol H_2 corresponds to 0.36 bar**. The pressure inside of the reactor was monitored during the course of the reaction and when the pressure dropped to a given value, the reaction was stopped by cooling the reactor in a water bath and releasing the remaining hydrogen gas. For entries 1 and 12 in **Table 1**, the hydrogen consumption was estimated by comparing the theoretically used H_2 based on 1H NMR with the amount used according to the pressure drop monitoring.

For Entry 1, partial hydrogenation was performed at 80°C under 8 bar H_2 . According to the 1H NMR, there are 20.8 %C=C left in the hPBD sample. This indicates that $20.8/25 = 83.2\%$ of the initial double bonds (C=C) are left

and that 16.8% of the C=C has been converted into single C-C, which corresponds to a **theoretical H₂ use** of 16.8%*2 mmol = **0.34 mmol H₂**.

For Entry 1, the reactor was charged to 8 bar of H₂. After 5 minutes of heating up to 80°C and simultaneous dissolution of the hydrogen, the pressure increased to 9.10 bar which was taken as the reference pressure. The reaction was stopped after 40 minutes when the display indicated 8.34 bar. This corresponds to a pressure difference of 9.10 - 8.34 = 0.55 bar, which corresponds to a **measured use of 0.15 mmol H₂** using the ideal gas law (see previous section):

$$\frac{0.55 \text{ bar}}{\frac{0.36 \text{ bar}}{0.1 \text{ mmol}}} = 0.15 \text{ mmol H}_2$$

For Entry 12 in **Table 1**, hydrogenation was performed at 40°C under 30 bar H₂. The same calculation as above gives a **theoretical use of 1.14 mmol H₂**. The initial pressure for this example was 30.5 bar. After 6h, the pressure dropped to 27.3 bar. Here the pressure difference is 30.5-27.3 = 3.2 bar which corresponds to a **measured use of 1.03 mmol H₂**:

$$\frac{3.20 \text{ bar}}{\frac{0.31 \text{ bar}}{0.1 \text{ mmol}}} = 1.03 \text{ mmol H}_2$$

For entries 1-6 (Low P, high T) and entries 7-13 (High P, Low T) in **Table 1**, the %C=C in the hPBD samples measured via ¹H NMR is plotted versus the measured use of H₂ via the pressure drop (**Figure S2**). In the plot, also the theoretical H₂ use for a certain hydrogenation degree of the hPBD is plotted. For the case of Low P & high T, there is quite a difference between the theoretical use and the measured use via the pressure drop, although the linear trendline has a R² of 0.97. However for the High P & Low T case, a good agreement between the measured data and the theoretical values is seen and the trendline has a R² of 0.98. While the pressure drop method does not fully match the theoretical H₂, it can be used as an experimental indication to estimate the %C=C in the hPBD samples.

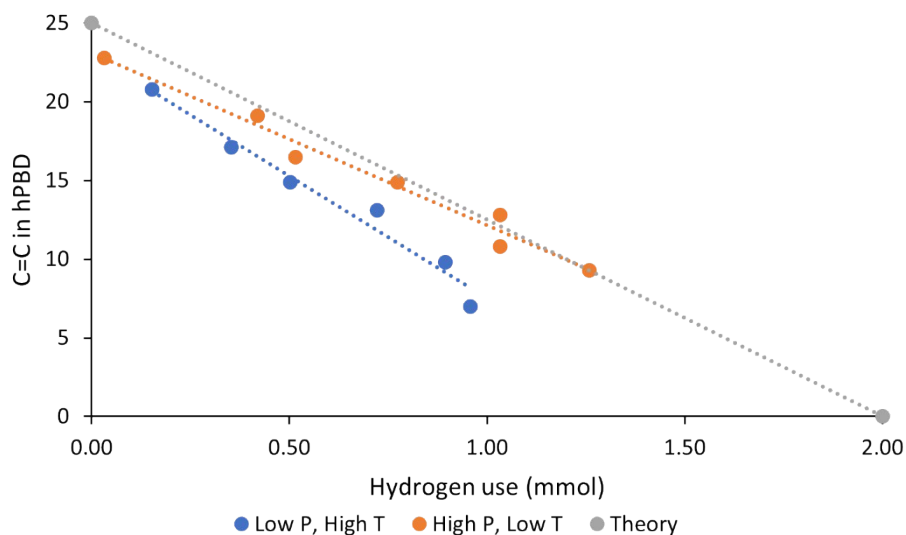


Figure S2. Plot of the H₂ use calculated via the pressure drop versus the %C=C in the hPBD samples determined via ¹H NMR for all entries in Table 1. The theoretical use indicates the case in which the use calculated via the pressure drop would be equal to the use calculated via ¹H NMR.

4. Characterization

4.1 GC analysis

GC analysis was performed on a Shimadzu GC-2010 Pro equipped with a CP Sil-5 CB column and an FID detector. 1 μ L sample was injected via a AOC-20i autosampler with a split ratio of 30. The N₂ carrier gas had a total flow of 76.6 mL/min. The temperature vs time profile was as follows: 8 min holding time at 35°C, ramp to 120°C with a rate of 7°C/min, a ramp to 280°C with a rate of 20°C/min, and lastly a holding time of 10 min at 280°C.

4.2 GCMS analysis

The GC 6890N was equipped with a HP-1MS ultra inert column. 1 μ L sample was injected with a split ratio of 30. The He carrier gas had a total flow of 1 mL/min. The temperature vs time profile was as follows: 4 min holding time at 40°C, ramp to 100°C with a rate of 5°C/min and a holding time of 2 min, a ramp to 280°C with a rate of 20°C/min and lastly a holding time of 5 min. The Agilent 5973N MSD was equipped with an electron impact ion source and a single quadrupole mass filter. A GC analysis was combined with a GCMS analysis to identify the compounds. The retention times of the C₇-C₃₀ n-alkanes in a standard mix were compared with the obtained retention times of the dienes to determine the chain lengths of products of C₁₅ or higher.

4.3 ¹H NMR analysis

High-field nuclear magnetic resonance (NMR) spectra were recorded on a Bruker Avance III HD 400 spectrometer with a Bruker Ascend™ 400 magnet system (¹H basic frequency of 400.17 MHz) and a 5 mm PABBO BB/19F-1H/D probe with z-gradients. All samples were dissolved in chloroform-d (CDCl₃). Data were recorded at room temperature using Bruker TopSpin 3.6.5 and processed and analyzed using Mestrenova 12.0.2. ¹H data were calibrated using tetramethylsilane (TMS) as an internal calibration reference.

Supporting data

1. Results heterogeneously catalyzed hydrogenation

Table S2. Results of PBD hydrogenation with heterogeneous catalysts. Conditions: 2 mL of a 1M PBD solution in THF, 4h, 80°C, 8 bar H₂.

Heterogeneous catalyst	Metal loading (mol%)	Degree of unsaturation in %C=C
5 wt% Pd/Al ₂ O ₃	0.125	24
5 wt% Ni/SiO ₂	0.125	25
5 wt% Ni/Al ₂ O ₃	0.125	25
66 wt% Ni/SiO ₂ -Al ₂ O ₃	0.800	25

2. HMW PBD characterization

The characteristics from the supplier (Sigma Aldrich)³ are given in **Table S3**.

Table S3. Characteristics of the used PBD as reported by the supplier.

Characteristic	Reported by supplier
Physical state	Rubber like solid
Density (25°C)	0.9 g/mL (lit.)
Weight	Average M_w 200,000-300,000
Viscosity	40, Mooney (lit.)
Glass transition T_g	-102°C
%Cis	98%

The ^1H spectrum (CDCl_3 , 400 MHz) of the PBD is displayed **Figure S3**. Two regions can be distinguished: protons associated with C=C double bonds can be found around 5.80 – 4.80 ppm, while protons associated with C-C single bonds are in the region of 2.40 – 0.70 ppm.⁴ Protons H_a (5.50 – 5.25 ppm) are connected to internally double bonded C-atoms from *cis*-1,4 and *trans*-1,4 units. 1,2-vinyl groups have 2 types of protons bonded to C=C bonds. The signal around 5.80 – 5.50 ppm corresponds to the methine protons H_b while the methylenic protons H_c have signals around 5.25 – 4.80 ppm. Allylic protons H_e in the chain between *cis*-1,4 and *trans*-1,4 units have signals at 2.40 – 1.8 ppm. Protons in the region 1.55 – 1.2 ppm are protons of the methylenic groups H_d from joint 1,2-vinyl groups or intrablock 1,2-units. Finally, the alkyl end groups ($-\text{CH}_3$) can be found around 1 – 0.70 ppm. The vinyl content (v) was calculated based on the following formula⁴

$$v = \frac{I_2}{I_1 + 0.5I_2}$$

with I_1 the sum of integrated intensities ($H_a + H_b$) and I_2 the integrated intensity H_c .

For the PBD, $I_1 = 43$ and $I_2 = 1$ so a vinyl content $v = \frac{1,0}{43,0 + 0,5} = 2.3\%$ was obtained, which is in agreement with the value reported by the supplier.

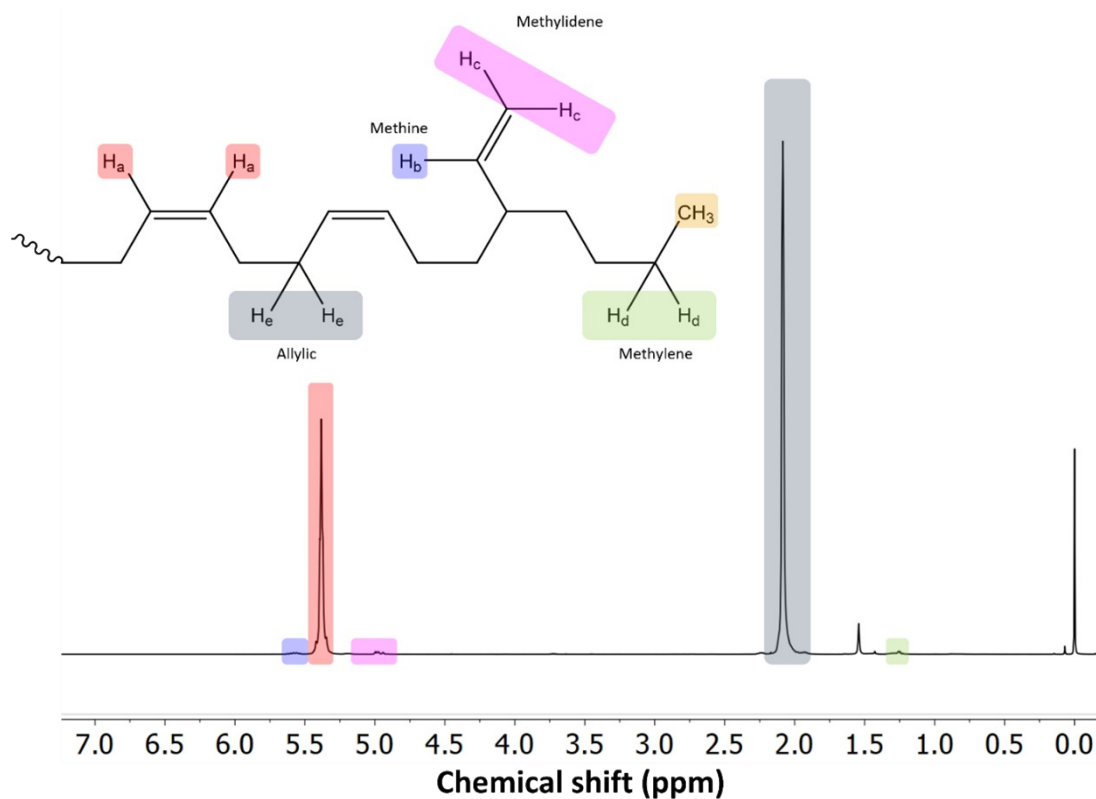


Figure S3. ^1H NMR spectrum of HMW PBD

3. Calculations hydrogenation and ethenolysis

To show how the data in **Table 1** on %C=C, conversion C=C after ethenolysis and %vinyl groups were calculated, step by step calculations are included for Entry 1 (representative for low P and high T hydrogenation) and Entry 12 (representative for high P and low T hydrogenation) of **Table 1**. For Entry 12, also the ^1H NMR spectra after partial hydrogenation (**Figure S4**) and ethenolysis (**Figure S5**) are included. In **Table S4**, NMR data after the partial hydrogenation of both samples are summarized and the NMR data after ethenolysis can be found in **Table S5**.

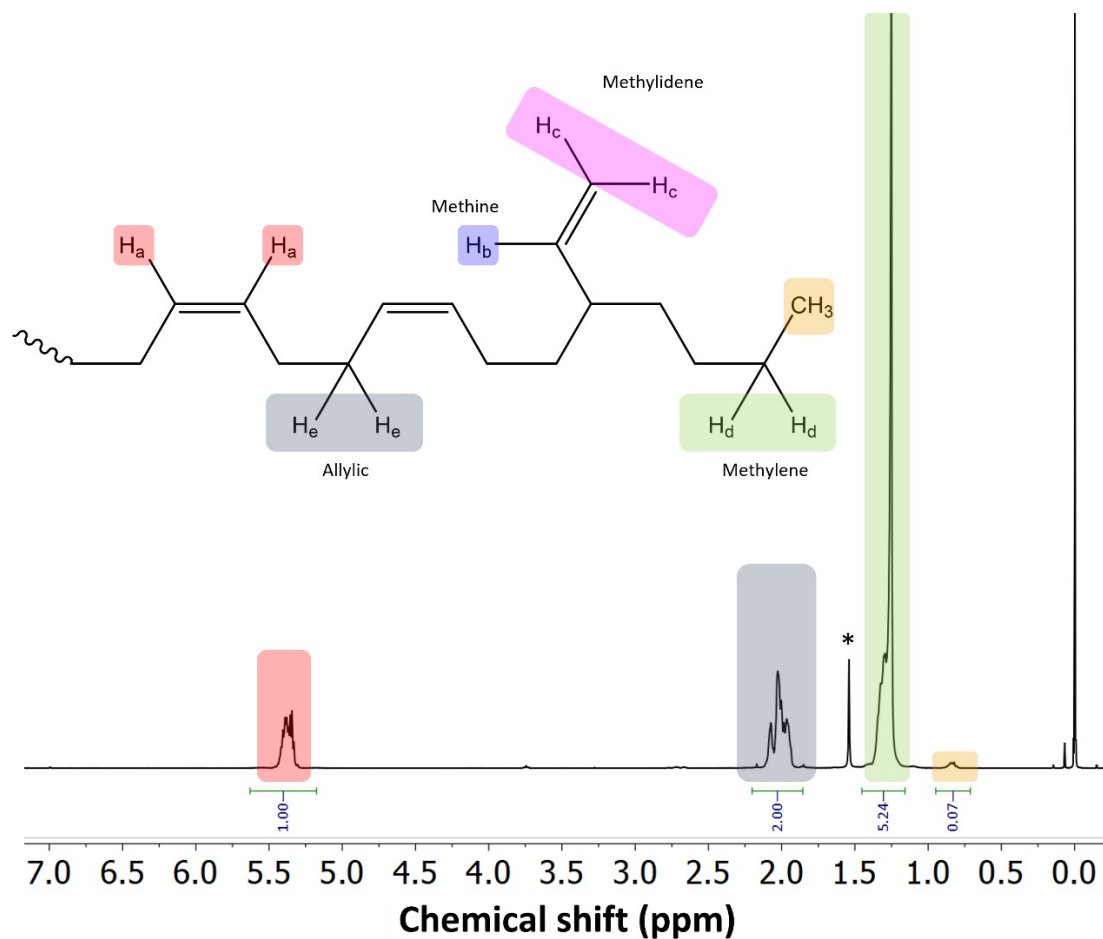


Figure S4. Entry 12, Table 1 after partial hydrogenation. *H₂O. Conditions: 2 mmol PBD in 2 mL THF, 0.125 mol% Ru(PPh₃)₃Cl₂, 40°C, 30 bar H₂.

Table S4. Summarized NMR data after partial hydrogenation of Entry 1 and 12 of Table 1.

Entry 1: Low P, high T

Proton	Shift (ppm)	#H per C	Signal NMR	Signal NMR/#H	% Signal
H _a	5.25-5.5	1	1.00	1.00	41.67
H _e	1.80-2.40	2	1.88	0.94	39.17
H _d	1.2-1.55	2	0.90	0.45	18.75
CH ₃	0.77-1	3	0.03	0.01	0.42

Total			3.81	2.4	100.0
Entry 12: High P, low T					
Proton	Shift (ppm)	#H per C	Signal NMR	Signal NMR/#H	% Signal
H _a	5.25-5.5	1	1.00	1.00	21.54
H _e	1.80-2.40	2	2.00	1.00	21.54
H _d	1.2-1.55	2	5.24	2.62	56.42
CH ₃	0.77-1	3	0.07	0.02	0.50
Total			8,31	4.64	100.0

To calculate the amount of C=C per 100C, all the signals were divided by their number of H-atoms per C-atom (Signal NMR/#H). From these values and their sum, the relative amount of the different C-atoms was calculated (% Signal). For Entry 1, the C-H_a signal was 41.67 % of the total integrated area, while for Entry 12, it was 21.54 %. To calculate the %C=C, these values need to be divided by 2 because 2 of these carbon atoms correspond to 1 double bond. This is then 41.67/2 = 20.83 or **20.8 %C=C** for Entry 1 and 21.54/2 = 10.77 or **10.8% C=C** for Entry 12.

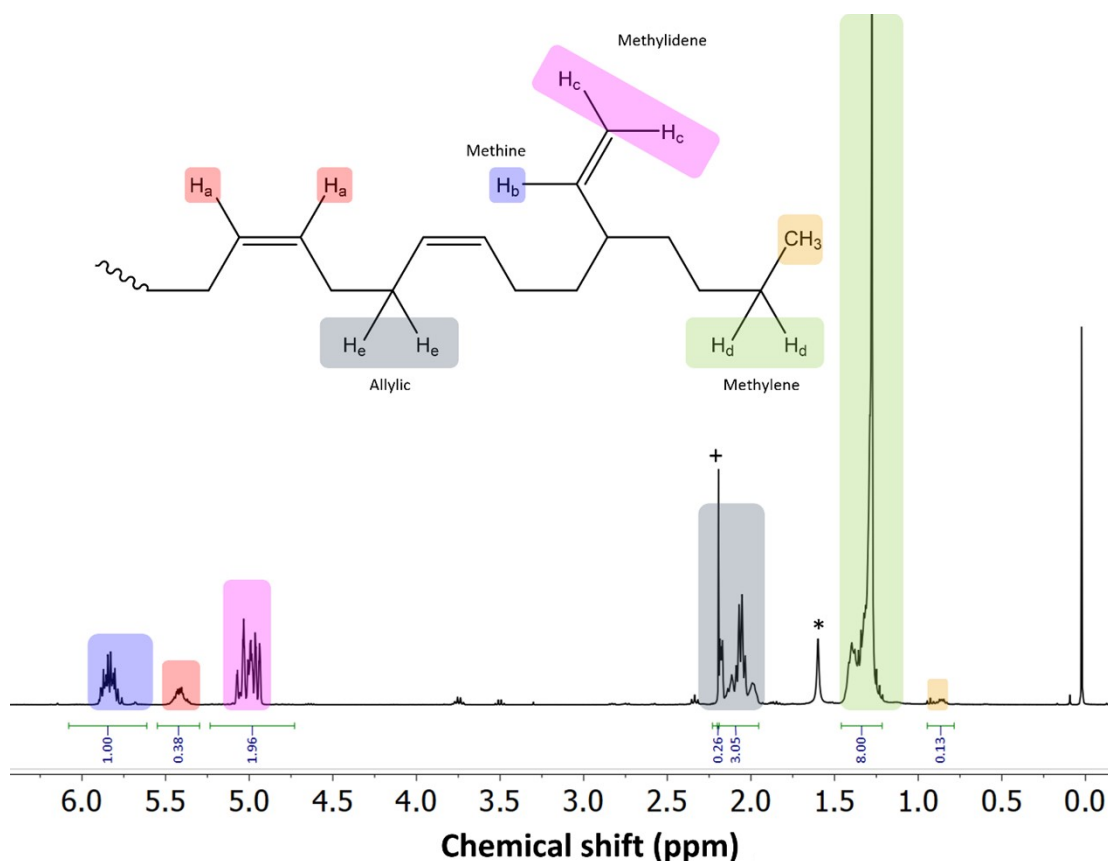


Figure S5. Entry 12, Table 2 after ethenolysis. *H₂O, *acetone (surface = 0.26). Protons H_e were corrected for the acetone peak overlap. Conditions: 0.1 mmol hPBD in 1 mL CDCl₃, 1 mol% Grubbs M220 catalyst, 2 mg BQ, 1h at 100°C, 8 bar C₂H₄.

Table S5. Summarized NMR data of Entry 1 and 12 after ethenolysis.

Entry 1					
Proton	Shift (ppm)	#H per C=C	Signal NMR	Signal NMR/#H	% Signal
H _b	5.5-5.8	1	1.00	1.00	25.83
H _a	5.25-5.5	1	0.13	0.13	3.36

H _c	4.8-5.25	2	1.86	0.93	24.02
H _e	1.8-2.4	2	2.20	1.10	28.41
H _d	1.2-1.55	2	1.39	0.70	17.95
CH ₃	0.7-1	3	0.05	0.02	0.43
Total			6.63	3.87	100.0

Entry 12

Proton	Shift (ppm)	#H per C=C	Signal NMR	Signal NMR/#H	% Signal
H _b	5.5-5.8	1	1.00	1.00	12.82
H _a	5.25-5.5	1	0.38	0.38	4.87
H _c	4.8-5.25	2	1.96	0.98	12.56
H _e	1.8-2.4	2	2.80	1.40	17.94
H _d	1.2-1.55	2	8.00	4.00	51.26
CH ₃	0.7-1	3	0.13	0.04	0.56
Total			14.27	7.80	100.0

To calculate the conversion of the internal C=C, the % signal of H_a was compared before and after ethenolysis. Conversion (X) was then calculated as

$$X = \frac{\%H_a \text{ before ethenolysis} - \%H_a \text{ after ethenolysis}}{\%H_a \text{ before ethenolysis}} \times 100\%$$

$$\text{In this case for Entry 1: } X = \frac{41.67 - 3.36}{41.67} \times 100\% = 92\%$$

$$\text{For Entry 12: } X = \frac{21.54 - 4.87}{21.54} \times 100\% = 77\%$$

The amount of vinyl groups after ethenolysis was calculated as %Signal of H_b. For Entry 1 this is 25.83 or **26%** and for Entry 12, this is 12.82 or **13%**.

4. Chromatogram of products detected under optimal non-isomerizing conditions

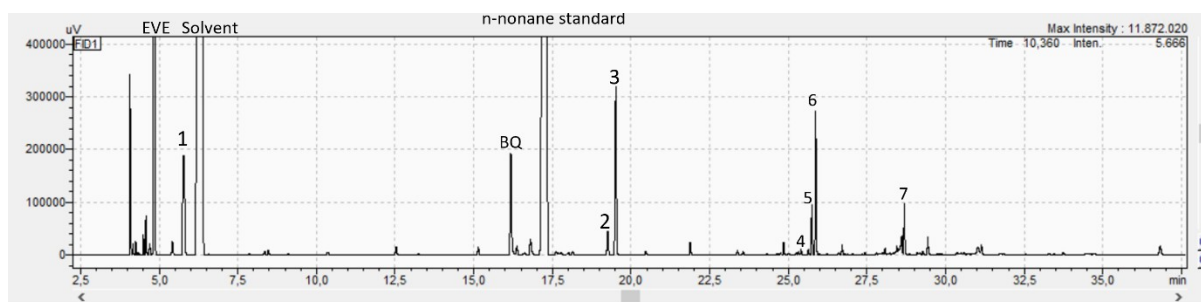


Figure S6. Chromatogram obtained for Entry 12, Table 1 as a representative product mixture with assignment for all peaks corresponding to >5% of the product selectivity. Identification based on GCMS, C_6 and C_{10} reference α,ω -dienes and a C_6 - C_{30} n -alkane standard mixture. Conditions: 0.1 mmol hPBD in 1 mL $CDCl_3$, 1 mol% Grubbs M220 catalyst, 2 mg BQ, 1h at $100^\circ C$, 8 bar C_2H_4 . EVE: ethyl vinyl ether; Solvent: $CDCl_3$; BQ: 1,4-benzoquinone; 1: 1,5-Hexadiene; 2: 1,5,9-Decatriene; 3: 1,9-Decadiene; 4: 1,5,9,13-Tetradecatetraene; 5: 1,5,13-Tetradecatriene; 6: 1,13-Tetradecadiene; 7: 1,17-Octadecadiene.

5. Product distributions isomerized fraction after ethenolysis

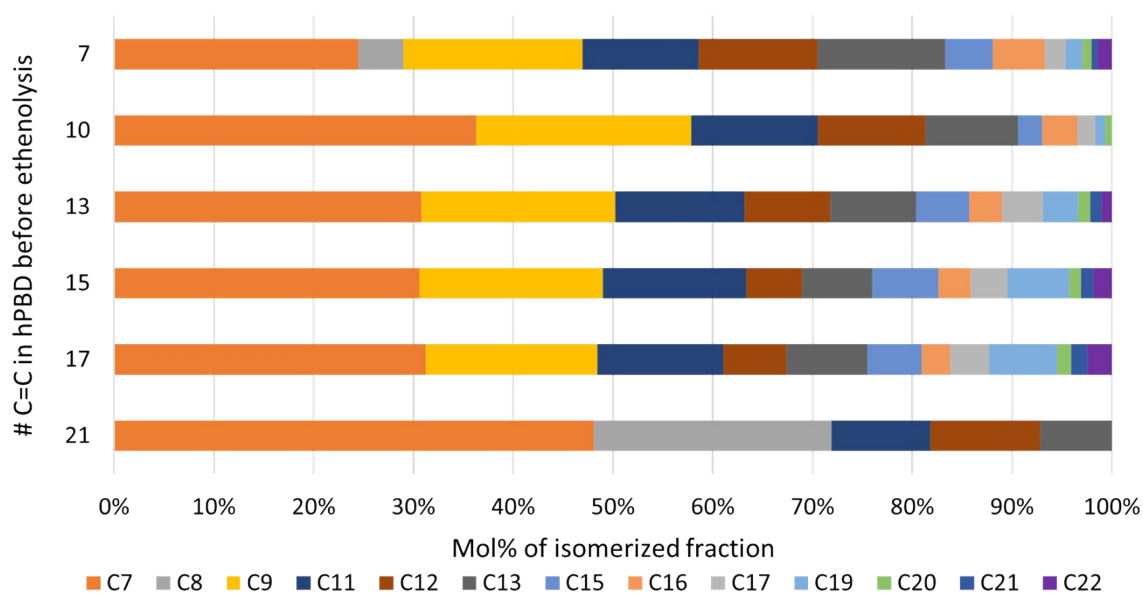


Figure S7. Product distributions of the isomerized fractions of entries 1-6 in Table 1. Conditions: 0.1 mmol hPBD in 1 mL CDCl_3 , 1 mol% Grubbs M220 catalyst, 2 mg BQ, 1h at 100°C, 8 bar C_2H_4 .

6. Large scale hydrogenation and ethenolysis

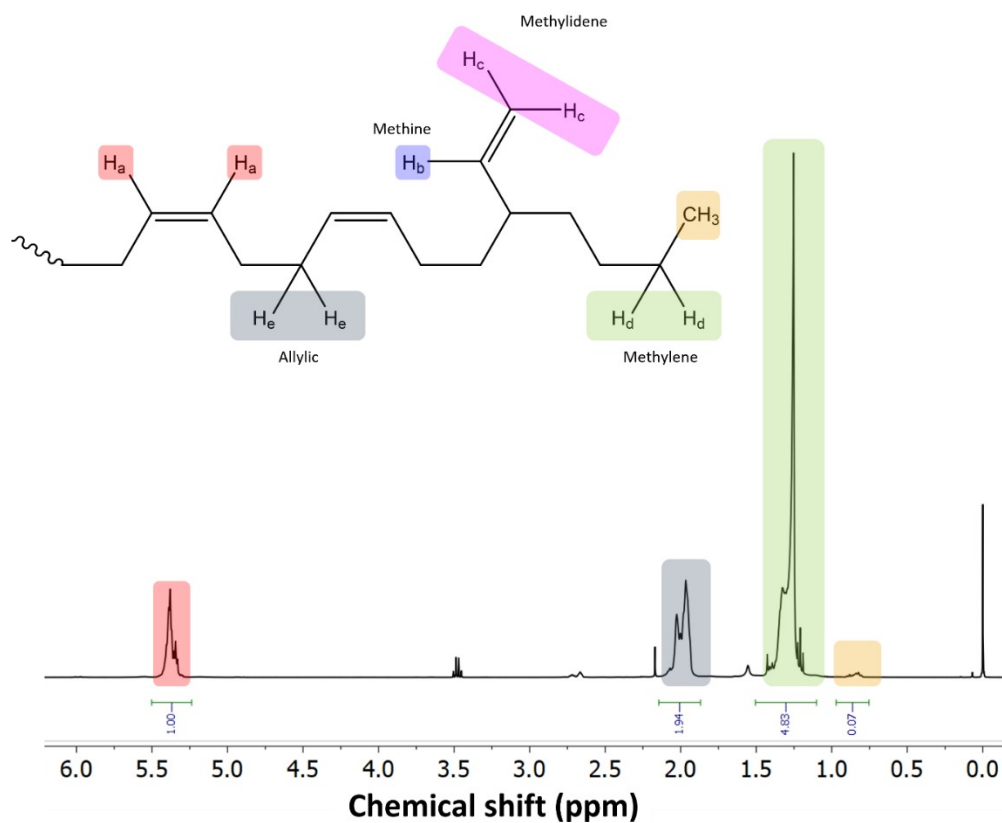


Figure S8. 1H NMR spectrum ($CDCl_3$) of large scale hydrogenated HMW PBD with 11% C=C. Conditions: 16.2 g PBD in 232 mL CPME, 0.125 mol% $Ru(PPh_3)_3Cl_2$ catalyst, 5h at 100°C, 14.5 bar H_2 .

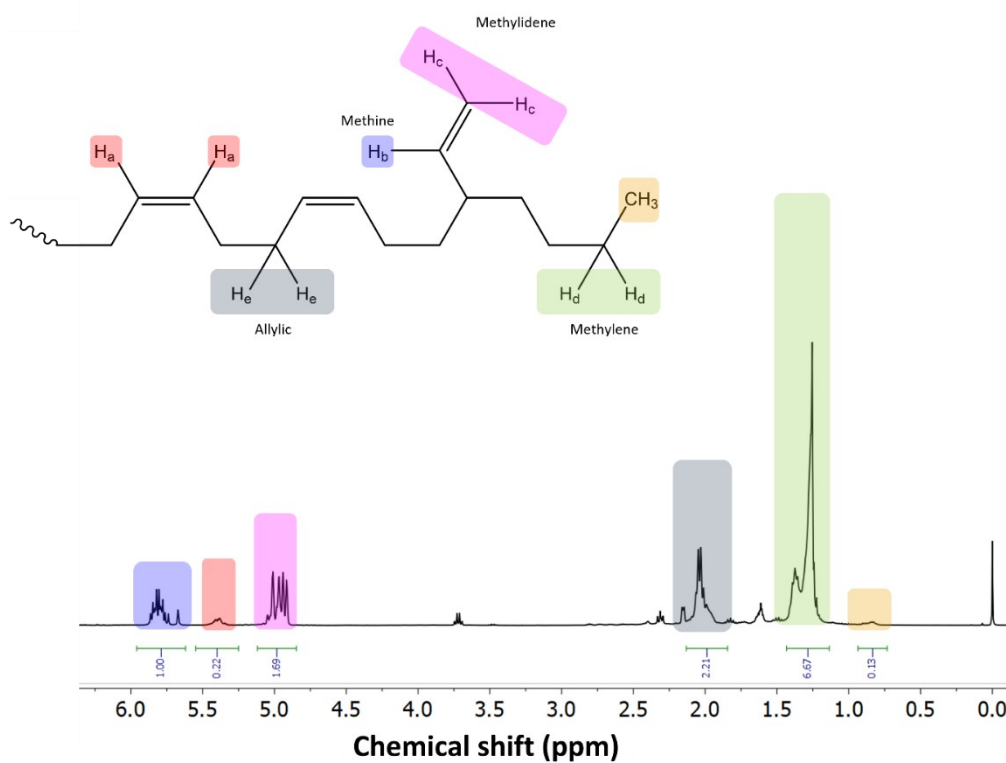


Figure S9. 1H NMR spectrum ($CDCl_3$) of large scale ethenolysis of hPBD with 11% C=C. Conditions: 1.5 g PBD in 30 mL $CDCl_3$, 0.57 mol% Grubbs M202 catalyst, 4h at 80°C, 8 bar C_2H_4 .

7. Mass recovery after hydrogenation

Table S6. Mass recovery after hydrogenation of HMW PBD in CPME. Conditions: 2.5 mL of 1.2M solution of PBD, 0.25 mol% $Ru(PPh_3)_3Cl_2$, 4h at 100°C.

Entry	H ₂ pressure (bar)	Product appearance after reaction	Initial mass (g)	Mass recovered (g)	% Recovery	%C=C
1	6	liquid	162	130.7	81	12.74
2	12	liquid	162	120.7	75	7.40
3	20	solid	162	145.4	90	6.10

8. One pot reaction

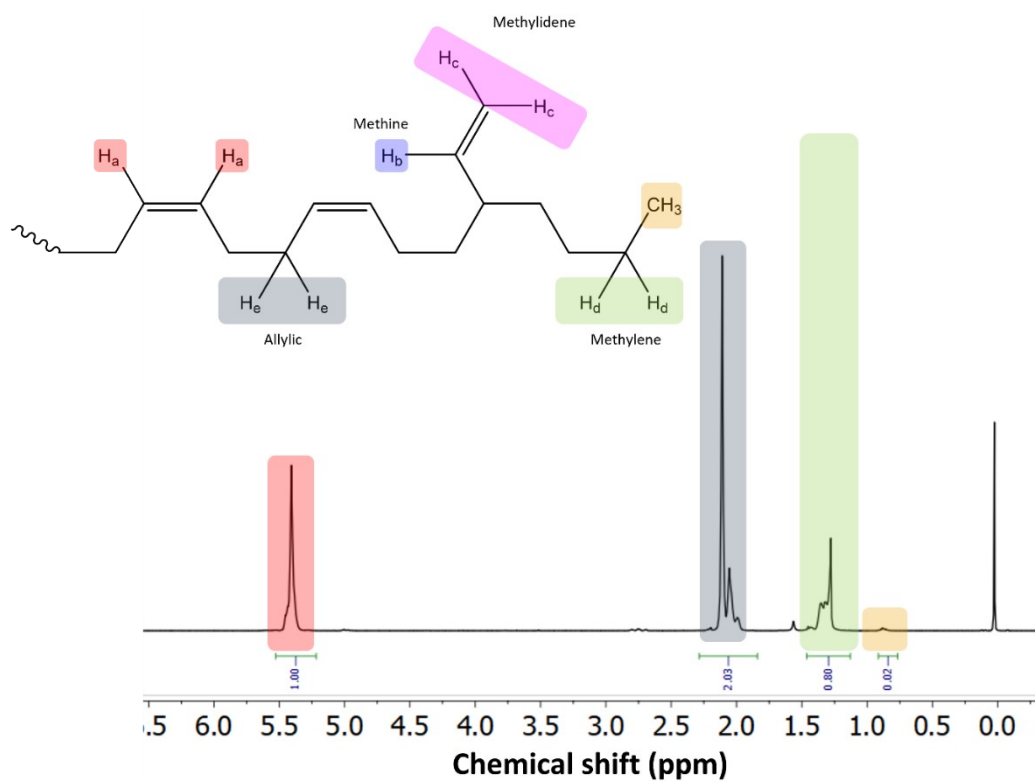


Figure S10. ^1H NMR spectrum after hydrogenation in the one pot hydrogenation-ethenolysis. Conditions: 2 mL of a 1 M solution of PBD in CDCl_3 , 0.125 mol% $\text{Ru}(\text{PPh}_3)_3\text{Cl}_2$ catalyst, 9 h at 40°C under 30 bar H_2 . The product contained 21% C=C.

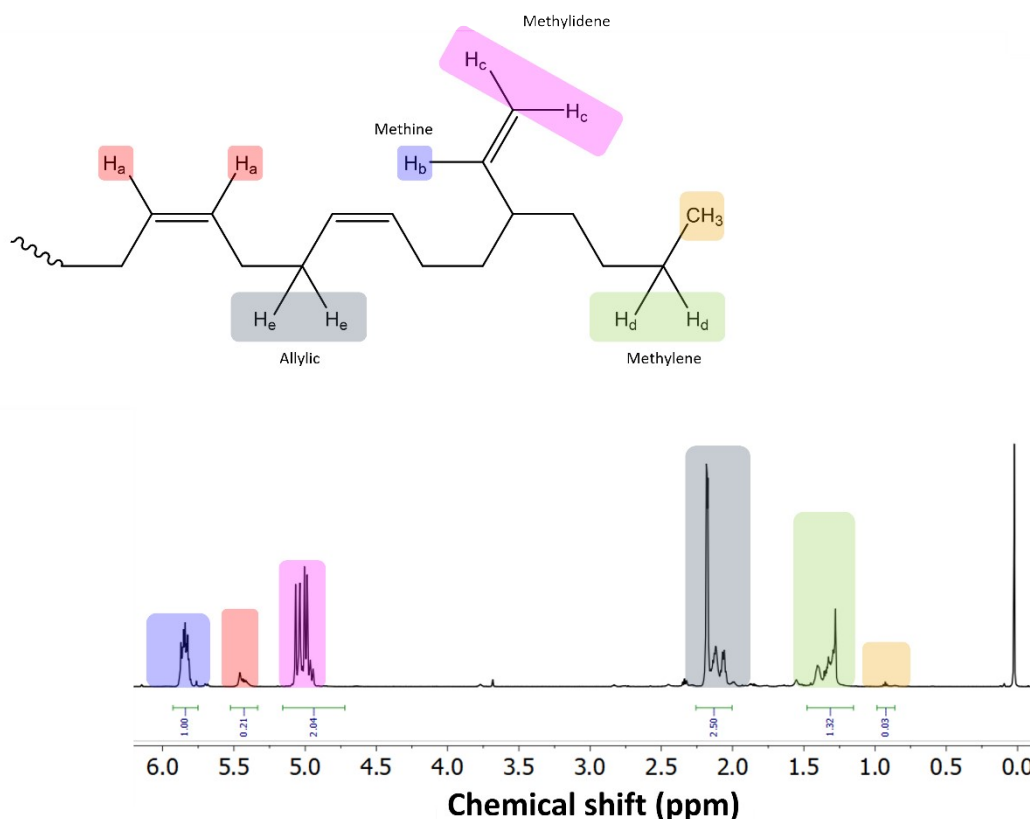


Figure S11. ^1H NMR spectrum after ethenolysis in the one pot hydrogenation-ethenolysis. Reaction conditions: 0.1 mmol hPBD in 1 mL CDCl_3 , 1 mol% Grubbs M220 catalyst, 2 mg BQ, 1 h at 100°C , 8 bar C_2H_4 , 81% conversion after ethenolysis.

9. Partial hydrogenation and ethenolysis of the rubber phase of high impact PS

Figure S12 depicts the ^1H NMR spectra of the starting rubber phase of the HIPS², the partially hydrogenated rubber phase and the spectrum after ethenolysis. It is clear that the amount of internal double bonds has decreased after the hydrogenation reaction and that ethenolysis creates terminal double bonds, indicating the formation of α,ω -dienes.

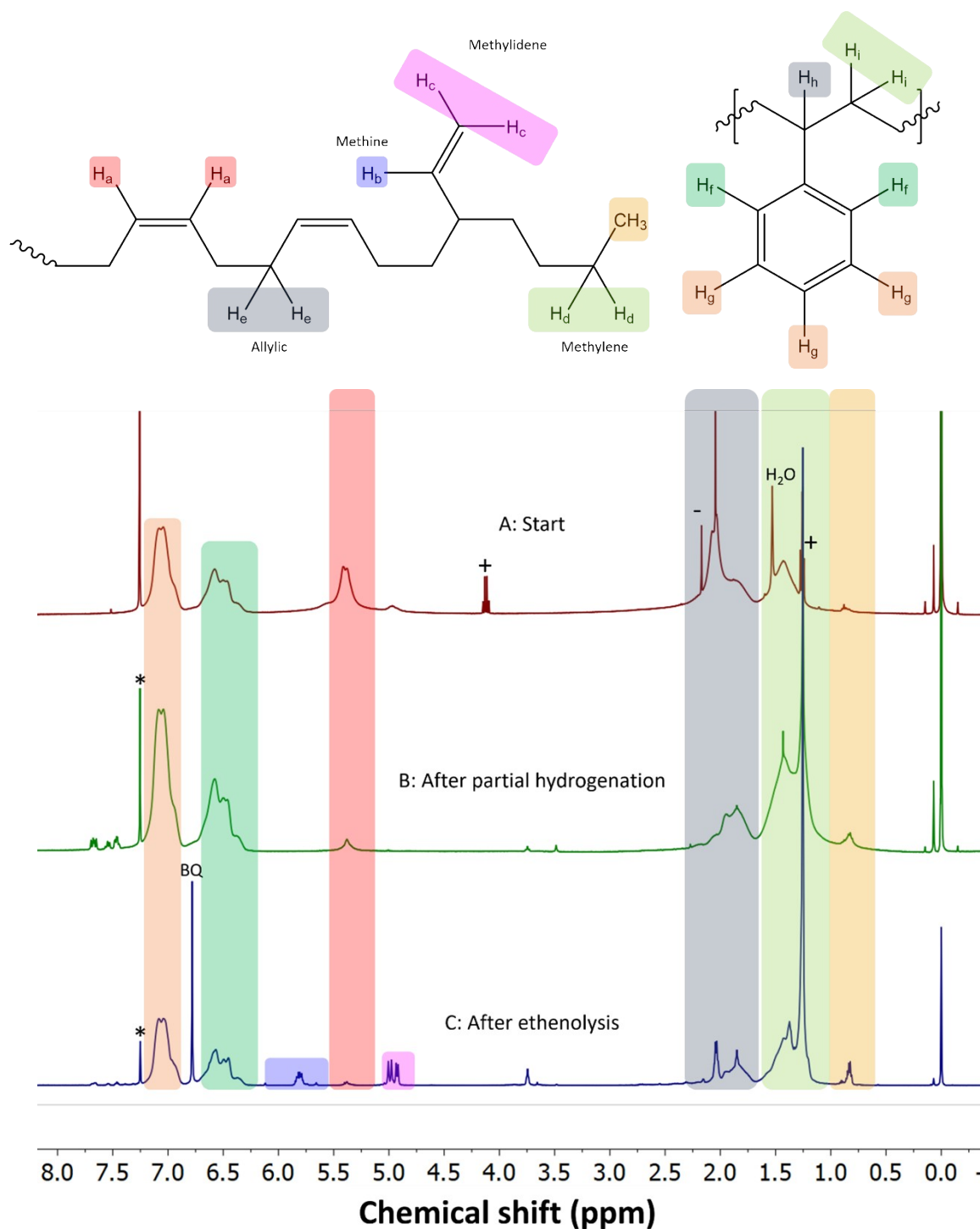


Figure S12. ^1H NMR spectra of the rubber phase of HIPS at the start, after partial hydrogenation and after ethenolysis. * CHCl_3 , $^+\text{EtOAc}$, $^-\text{Acetone}$. Conditions partial hydrogenation: 72 mg rubber phase of HIPS in 2 mL THF (0.5 mmol C=C), 12 bar H_2 , 0.5 mol% $\text{Ru}(\text{PPh}_3)_3\text{Cl}_2$ (4.8 mg), 2h; conditions ethenolysis: 30 mg hydrogenated HIPS rubber in 1 mL CDCl_3 , 1 mg Grubbs M220, 2 mg BQ, 1h, 100°C , 8 bar C_2H_4 .

10. Cross-metathesis

The expected products of CM of hPBD with DMM can also be made by CM of 1,5-hexadiene (C₆), 1,9-decadiene (C₁₀), 1,13-tetradecadiene (C₁₄), ... To estimate the retention times of the products on GC and identify the signals in the ¹H NMR spectrum, CM with DMM using 1,5-hexadiene and 1,9-decadiene was performed.

GC analysis

In **Figure S13A**, the GC chromatogram of a dummy mixture of the reagents 1,5-hexadiene, 1,7-octadiene, 1,9-decadiene and 1,11-dodecadiene is displayed. CM was performed only with 1,5-hexadiene (**Figure S13B**) and 1,9-decadiene (**Figure S13C**). It is clear that no substrate is left after reaction and 2 product peaks are detected which are hypothesised to be *cis/trans*-isomers. For the CM of hPBD (17% C=C), product peaks have comparable retention times as can be seen in **Figure S13D**.

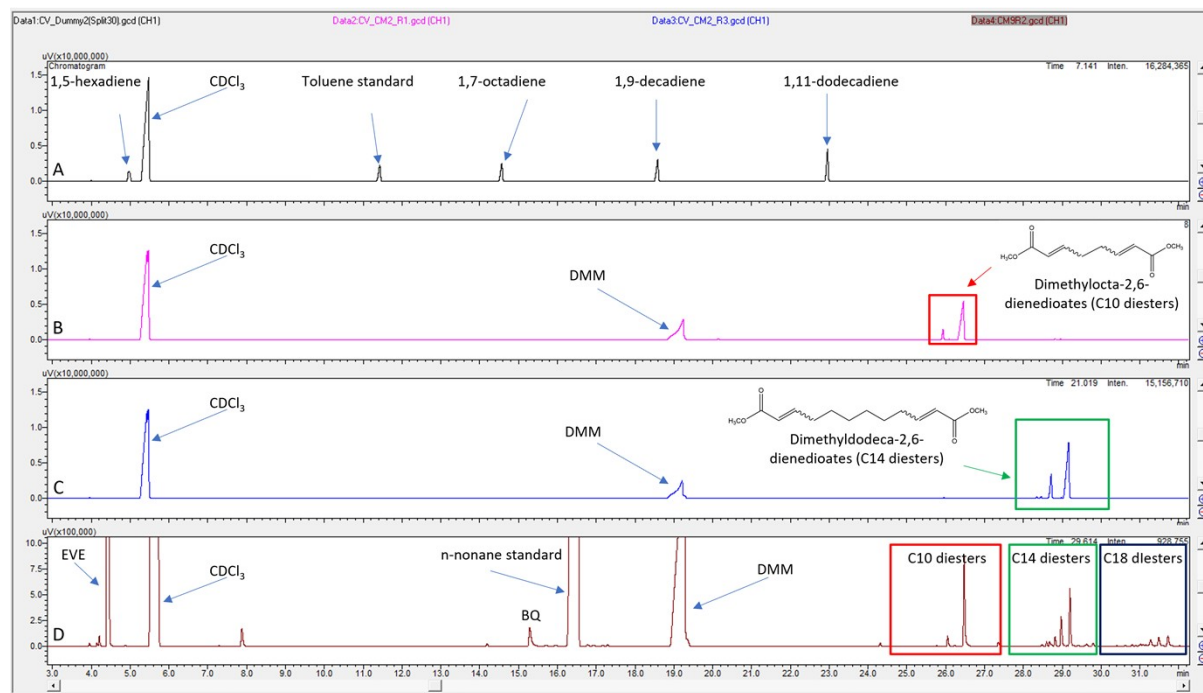


Figure S13. GC Chromatograms of dummy mixture of C₆, C₈, C₁₀ and C₁₂ dienes (A), CM of 1,5-hexadiene and DMM (B), CM of 1,9-decadiene and DMM (C) and after CM of hPBD with DMM (D). All chromatograms were shifted slightly to overlap the DMM peak.

NMR analysis

The following **Table S8** gives an overview of the reported shifts and J coupling values.⁵ These were compared to the peaks in the ¹H NMR spectra to identify which peaks in the overlap region at 5.8 ppm belong to the diester proton H_a and which are from the MA. J(a,b) was determined to be 0.039 ppm based on the multiplet at 6.94 ppm. The insets in **Figure S14A** and **Figure S14B** show the assignments.

Table S7. Shifts and J coupling values of methyl acrylate (MA)

Proton	Shift (ppm)	J coupling values (Hz)
H _e	6.4	J(e,f) 17.4 Hz
H _f	6.12	J(e,d) 1.4 Hz
H _d	5.82	J(f,d) 10.5 Hz
-OCH ₃	3.76	

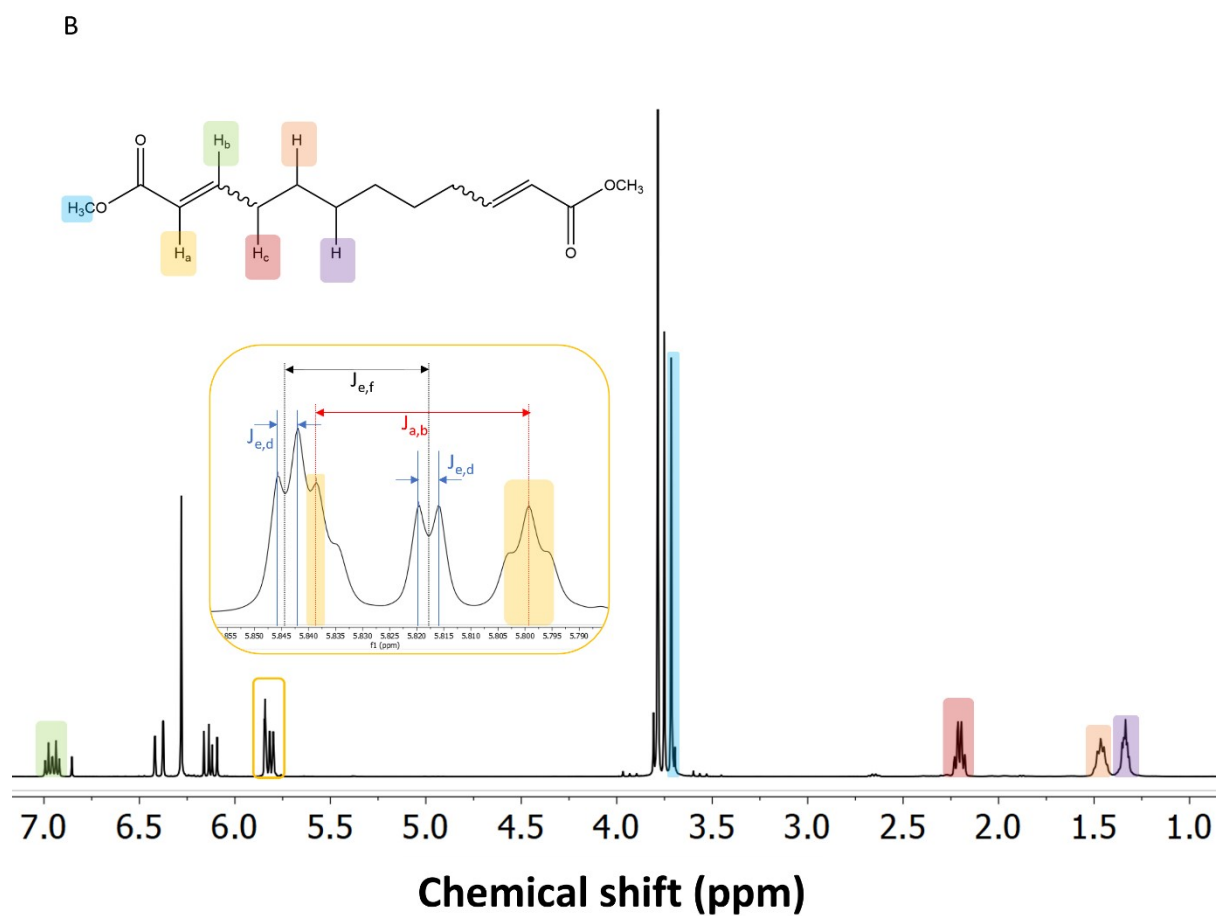
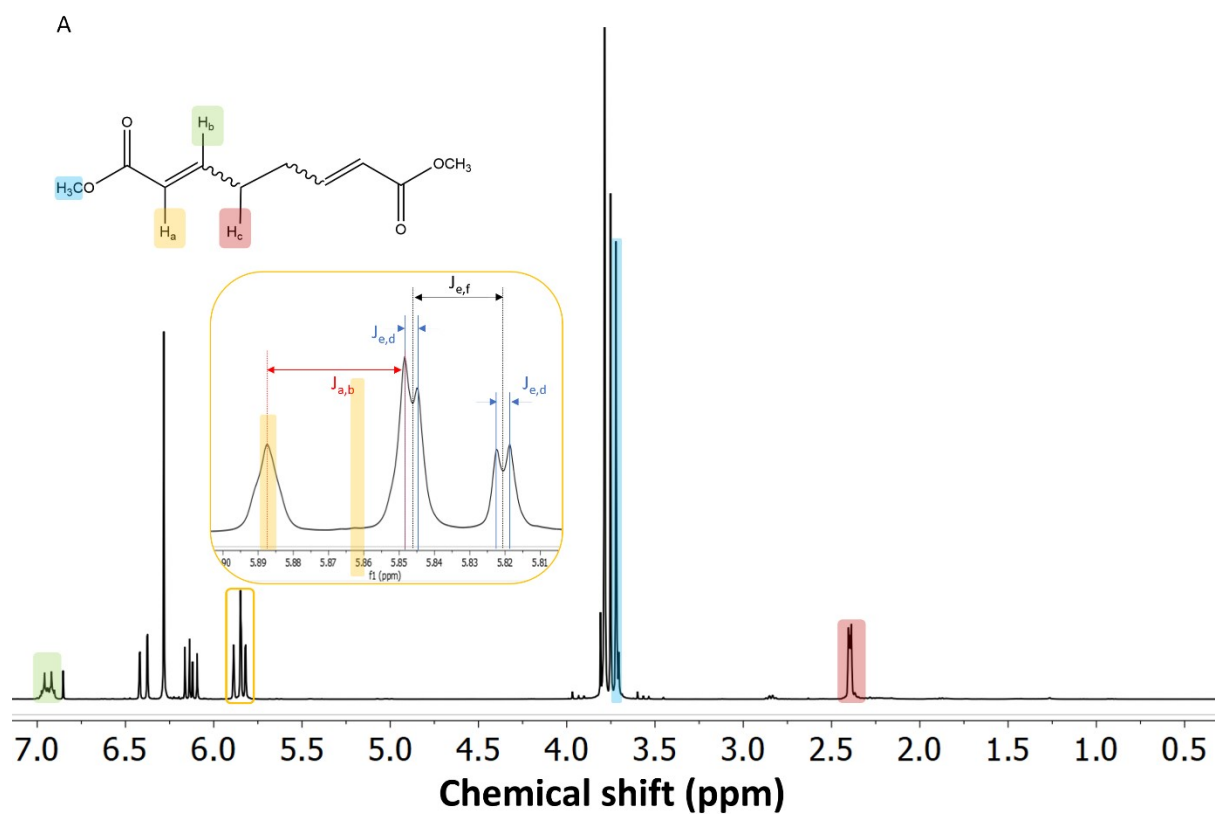


Figure S14. 1H NMR spectrum of CMM reaction of 1,5-hexadiene with DMM (A) and of 1,9-decadiene (B).

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