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# Converting natural rubber waste into Ring-opening Metathesis polymers with oligo-1,4-cis-isoprene sidechains

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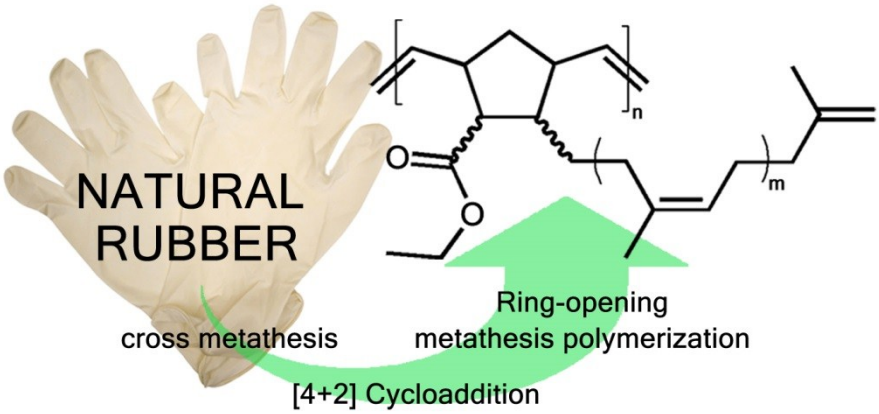
## ELECTRONIC SUPPORTING INFORMATION



**General**

Nuclear magnetic resonance experiments were done on a Bruker Avanze 300 MHz spectrometer ($^{1}H$: 300.36 MHz; $^{13}C$: 75.53 MHz) at 25 °C. Chemical shifts are given in ppm relative to a tetramethylsilan (TMS) standard. Deuterated solvents were obtained from Cambridge Isotope laboratories Inc. and spectra were referenced against the residual proton signals according to literature.[1]

GC-MS analyses were carried out on an Agilent Technologies 7890A GC system equipped with a 5975C mass selective detector (inert MSD with Triple Axis Detector system, EI, 70 eV). Samples were injected by employing autosampler 7683B in a split mode 1/25 (inlet temperature: 250 °C; injection volume: 0.1 µL) and separated on an Agilent Technologies J&W GC HP-5MS capillary column (30 m x 0.2 mm x 0.25 µm) at a constant helium flow rate (He 5.0 (Air Liquide), 1.000 mL/min, average velocity 36.5 cm/sec). A general gradient temperature method was used (initial temperature: 50 °C for 1 min, linear increase to 300 °C (40 °C.min$^{-1}$), hold for 1 min, 1 min post-run at 300 °C, detecting range: 50.0-550.0 amu, solvent delay of 2.80 min).

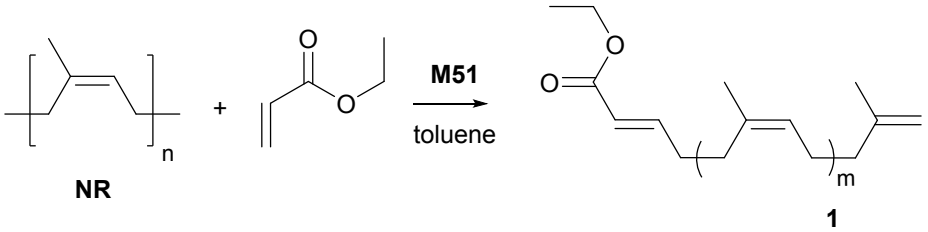
Differential scanning calorimetry (DSC) analyses were measured on a DSC 8500 instrument from Perkin Elmer in a temperature range from -20 to 100°C with a heating rate of 20°C/min for the first run and with 20°C/min in the second run ($T_g$ values were retrieved from the second heating run).

Thermogravimetric analyses (TGA) were performed with a Netzsch Simultaneous Thermal Analyzer STA 449C (crucibles: aluminium from Netzsch). A helium flow of 35 mL min$^{-1}$ was used in combination with a protective flow of helium of 8 mL min$^{-1}$. The heating rate until a final temperature of 550 °C was 10 °C min$^{-1}$.

Gel permeation chromatography (GPC) was carried out on a system provided by WGE Dr. Bures operated with THF (separating columns from MZ-Gel SD plus, linear 5µ; UV und RI detector SEC 3010). Poly(styrene) standards purchased from Polymer Standard Service were used for calibration.

[1] Fulmer, G. R.; Miller, A. J. M.; Sherden, N. H.; Gottlieb, H. E.; Nudelman, A.; Stoltz, B. M.; Bercaw, J. E.; Goldberg, K. I. *Organometallics* **2010**, *29*, 2176.

**Degradation of natural rubber gloves**




2.01 g natural rubber gloves (Kimtech PFE Cat. III AQL 1.5; i.e. approx. 29.5 mmol double bonds) of finely chopped rubber gloves were put in a 100 mL Schlenk tube equipped with a magnetic stirrer bar under nitrogen atmosphere and suspended in 40 mL of toluene (Sigma Aldrich, 99.9%). After 25 min ethyl prop-2-enoate (ethyl acrylate , Fluka, >99%; 15 mL, 13.8 g, 138 mmol, 4.7 eq. in respect to double bonds) was added and the reaction mixture was heated to 80°C. After 2 h 98.6 mg of **M51** (0.151 mmol, i.e. 0.5 mol% in respect to double bonds) was added and the reaction mixture was heated at 80°C for 22 h. After cooling down, ethyl vinyl ether (0.2 mL) was added and the reaction mixture was stirred for further 20 min. After that, insoluble parts were removed by filtration and volatile parts of the filtrate were removed using a rotary evaporator. The brown oily residue was finally dried under vacuum until constant weight was reached. The raw product was characterized by four spots on a thin layer chromatogram (eluent: cyclohexane:ethyl acetate = 15:1, staining with $KMnO_4$) with the following retention factors: $R_{f1}$=0.34, $R_{f2}$=0.60, $R_{f3}$=0.64, $R_{f4}$=0.94.
Crude yield: 3.24 g (162% in relation to mass of natural rubber; 65% in relation to full conversion towards ethyl 6-methylhepta-2,6-dienoate ($C_{10}H_{16}O_2$; MW: 168.24)).

Purification was done by column chromatography (eluent: cyclohexane:ethyl acetate = 15:1; 600 mL silica) and gave
*a first fraction* of 78.5 mg of a transparent oil ($R_f$=0.94),
*a second fraction* of 1.85 g (yield: 37 % in relation to full conversion towards ethyl 6-methylhepta-2,6-dienoate,) of a yellowish oil ($R_f$=0.64-0.60). $^1$H-NMR revealed **1** wit m = 3.2 and E/Z = 92/8. The theoretical yield for $\mathbf{1}_{m=3.2}$ is 2.70 g, accordingly 69 m% was found in this fraction.
*a third fraction* of 268 mg ($R_f$=0.34) of a yellowish oil which slowly solidifies, identified as diethyl but-2-enedioate

**Degradation of natural rubber**
The procedure described above was followed using 2.00 g natural rubber, 30 mL toluene, 15 mL ethyl prop-2-enoate and 97.7 mg **M51**.
Crude yield: 3.61 (180% in relation to mass of natural rubber; 73% to full conversion towards ethyl 6-methylhepta-2,6-dienoate). A $^1$H-NMR spectrum of the crude reaction mixture is shown in Fig. S1.

After purification as described above the following fractions were obtained:
*first fraction* of 59.5 mg of a transparent oil ($R_f$=0.94)
*second fraction* of 2.05 g (yield: 41 % in relation to full conversion towards ethyl 6-methylhepta-2,6-dienoate) of a yellowish oil ($R_f$=0.64-0.60). $^1$H-NMR revealed **1** with m = 3.0 and E/Z = 92/8. The theoretical yield for $\mathbf{1}_{m=3.0}$ is 2.74 g, accordingly 75 m% was found in this fraction.
*third fraction* of 535 mg ($R_f$=0.34) of a yellowish oil which slowly solidifies, identified as diethyl but-2-enedioate

**Influence of reaction conditions in particular catalyst loading**
Reactions were performed as described above with changes according to Table S1. Every try was done with 2 g natural rubber (or natural rubber gloves). The crude yield is the weight of the residue after removing volatiles. The crude products were investigated using $^1$H-NMR spectroscopy. The integral for the peak at 5.83 ppm was set to 1 and the integral for the peak at 5.24-5.05 ppm was read out as factor m (i.e. repeating units of oligo(isoprene), see drawing above. Further, the peak at

6.83 ppm was integrated and its integral was divided by 2 giving the ratio of diethyl fumarate to equivalents of **1** with the m as determined above. This value was used to calculate a percental ratio of **1** : diethyl fumarate given in Table S1 last column. Further, mol-percent were converted to mass-percent and with that the weight of **1** (with given m) within the crude product was calculated and is given in the next to last column.

**Table S1** Degradation of 2 g natural rubber under different reaction conditions

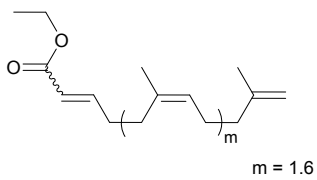
| Entry | M51 [mol%] | Time [h] | m [a] | Crude Yield [g] [b] | Crude Yield without Fumarate [g] [c] | 1 : Fumarate [%] [d] |
|---|---|---|---|---|---|---|
| 1 | 1.1 | 16 | 1.6 | 4.36 | 3.81 | 81 : 19 |
| 2 | 0.2 | 16 | 14.5* | 1.51 | 1.39 | 63 : 37 |
| **3** | **0.5** | **16** | **3.0**** | **3.61** | **3.19** | **78 : 22** |
| 4 | 0.5 | 5 h | 5.3 | 2.12 | 1.70 | 57 : 43 |
| 5 | 0.5 | 3 + 5 [e] | 3.7 | 2.94 | 2.71 | 83 : 17 |
| 6 | 0.5 | 32 | 3.1 | 3.66 | 2.81 | 60 : 40 |
| 7 [f] | 0.5 | 16 | 2 | n.d. | n.d. | 79 : 21 |
| **8 [g]** | **0.5** | **16** | **3.2** | **3.24** | **2.59** | **64 : 46** |
| 9 [g] | 2 | 16 | 0.8 | 3.54 | 2.27 | 58 : 42 |
| 10 [h] | 1 | 16 | 2.8 | 5.62 | 2.66 | 31 : 69 |
| 11 [h] | 0.5 | 16 | 3.4 | 2.96 | 2.26 | 59 : 41 |
| 12 [i] | 0.5 | 16 | n.d. | n.d. | n.d. | n.d. |

[a] m is the average number of isoprene repeating groups according to the drawing above; b crude yield describes the weight of the residue after removal of the volatiles; [c] calculated share of **1** with a given m in the crude product; [d] molar ratio of **1** to *E*-fumarate according to $^1$H-NMR; [e] the reaction mixture was first reacted at 80°C without ethyl acrylate for 3 h, afterwards ethyl acrylate was added and the reaction was reacted at 80°C for further 5h; [f] the crude reaction product from entry 4 was used as starting material; [g] in this case natural rubber gloves (i.e. vulcanized NR) were used instead of natural rubber; [h] methyl acrylate was used instead of ethyl acrylate; [i] reaction performed without acrylate, the residue was analyzed by GPC (THF): $M_n$ = 48000 g/mol, $M_w$ = 90000 g/mol; * GPC (THF): $M_n$ = 1800 g/mol, $M_w$ = 4000 g/mol; ** GPC (THF): $M_w$ < 500 g/mol

**Characterization of representative fractions**

*Fraction 1* ($R_f$=0.94) was not comprehensively characterized but contained mainly species bearing oligoisoprene units as evident from NMR-spectroscopic investigations (Figs S2-S3).

*Fraction 2* ($R_f$=0.60, **1**) represents the main fraction and contains oligoenoates in this case with on average 1.6 units m (according to the drawing) and an E/Z ratio of the 2-enoatic double bond of about 97:3 as evident from NMR-spectroscopic investigations (Figs S9-S13). GC-MS investigations confirmed the presence of species with m=0 until m=4 (Figs S4-S8). Spectra in accordance to literature.[1]




$^1$H-NMR (δ, $CDCl_3$, 300 MHz): 6.98 (dt, 0.97H, -C*H*$^{trans}$=CH-COOEt), 6.19 (m, 0.03H, -C*H*$^{cis}$=CH-COOEt), 5.83 (d, $^3J_{HHtrans}$ = 15.6 Hz, 1H, -CH$^{trans}$=C*H*-COOEt – submersed –CH$^{cis}$=C*H*-COOEt); 5.24-5.05 (m, 1.59H, -C($CH_3$)=C*H*-); 4.70, 4.66 (s, 2H, -C($CH_3$)=C$H_2$), 4.17 (q, 2H, COOC$H_2$$CH_3$); 2.33-1.96 (m, 10.8H, -$CH_2CH_2$-); 1.71, 1.67 (2x s, 8H, -C(C$H_3$)=CH-, -C(C$H_3$)=C$H_2$); 1.27 (t, 3H, COOCH$_2$C$H_3$).

$^{13}$C{$^1$H}-NMR (δ, $CDCl_3$, 75 MHz): 166.7 (1C, -*C*OOEt); 148.8 (1C, -*C*H$^{trans}$=CH-COOEt), 145.9, 145.7 (q, -*C*(C$H_3$)=$CH_2$), 135.3, 135.1, 133.8 (-*C*($CH_3$)=CH-), 126.3, 126.1, 125.4, 125.2, 125.0 (-C($CH_3$)=*C*H-), 121.6 (2C, -*C*H$^{trans}$=CH-COOEt), 110.1, 109.9 (-C($CH_3$)=*C*$H_2$), 60.3 (COO*C*H$_2$CH$_3$), 38.2, 38.0 (-*C*H$_2$-C($CH_3$)=$CH_2$), 32.3, 32.2, 32.1, 30.9, 30.8, 30.5 (-*C*H$_2$CH$_2$-C($CH_3$)=CH-), 26.5, 26.3, 26.2 (-*C*H$_2$-C($CH_3$)=CH-), 23.5, 23.35, 23.29, 22.61, 22.57 (-C(*C*H$_3$)=CH-, -C(*C*H$_3$)=$CH_2$), 14.4 (COOCH$_2$*C*H$_3$).

Fraction 3 ($R_f$=0.34) was identified as the product from homo-dimerization of ethyl prop-2-enoate, namely diethyl but-2-enedioate (diethylfumerat), see Figs S14-S15).

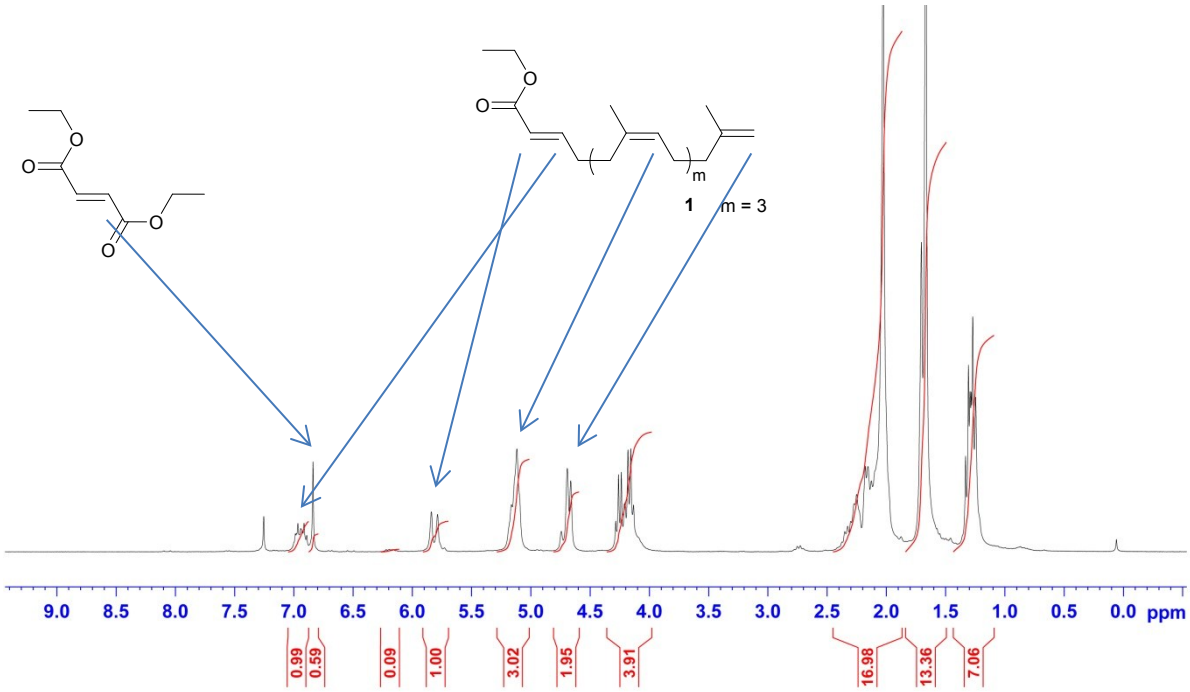



**Fig. S1**. $^1$H-NMR of the crude natural rubber degradation product mixture.

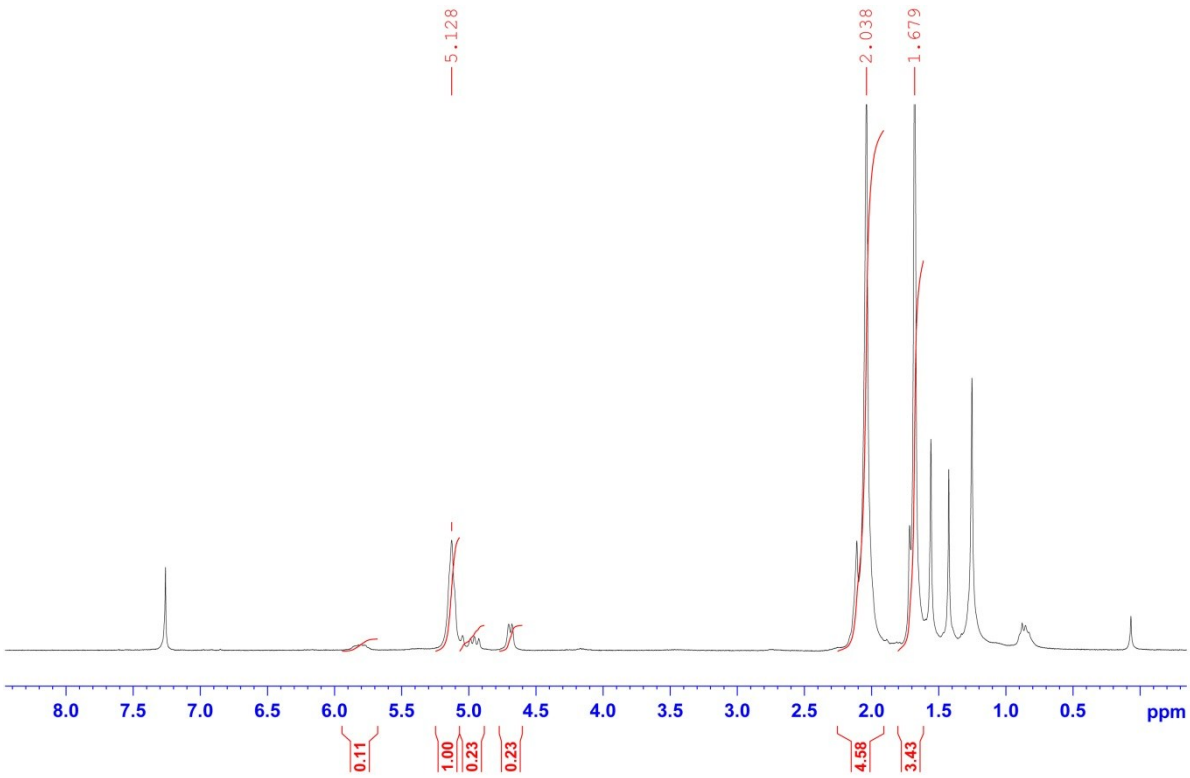



**Fig. S2**. $^1$H-NMR of *fraction 1* from the natural rubber degradation experiment

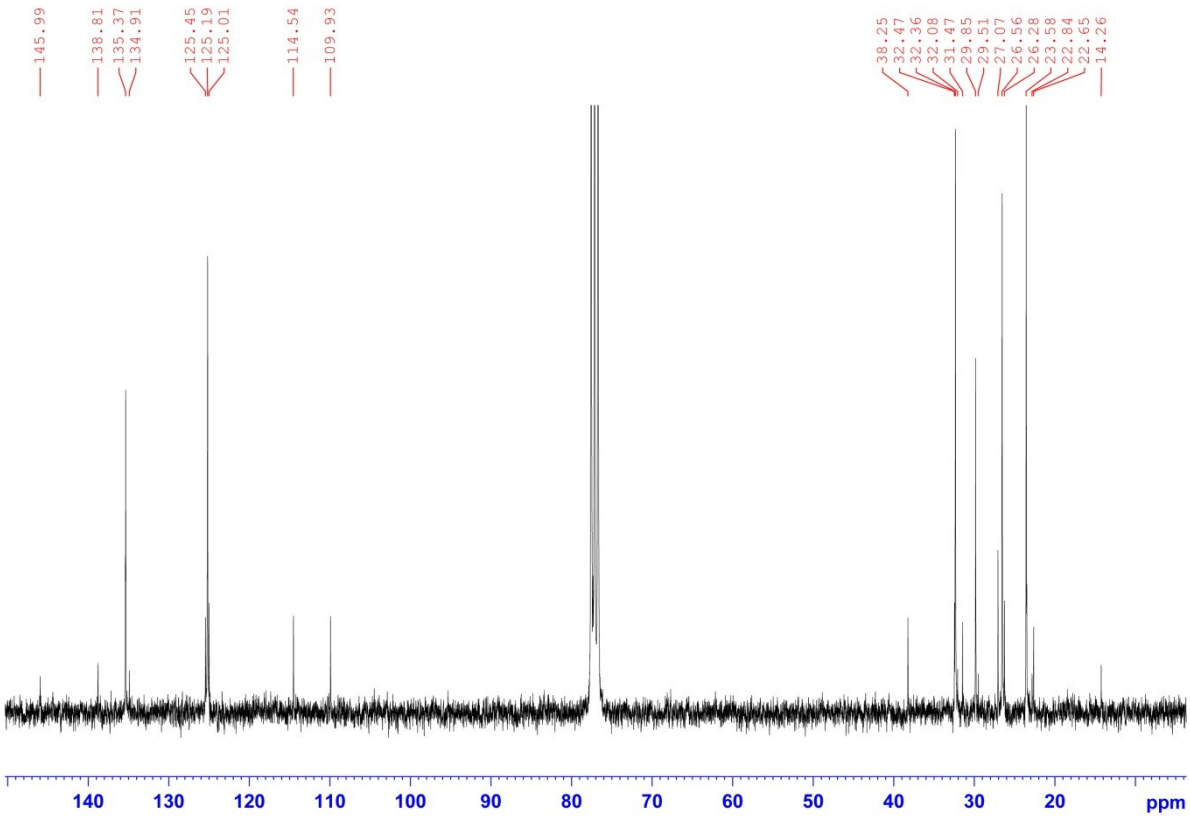



**Fig. S3**. $^{13}C\{^{1}H\}$-NMR of *fraction 1* from the natural rubber degradation experiment

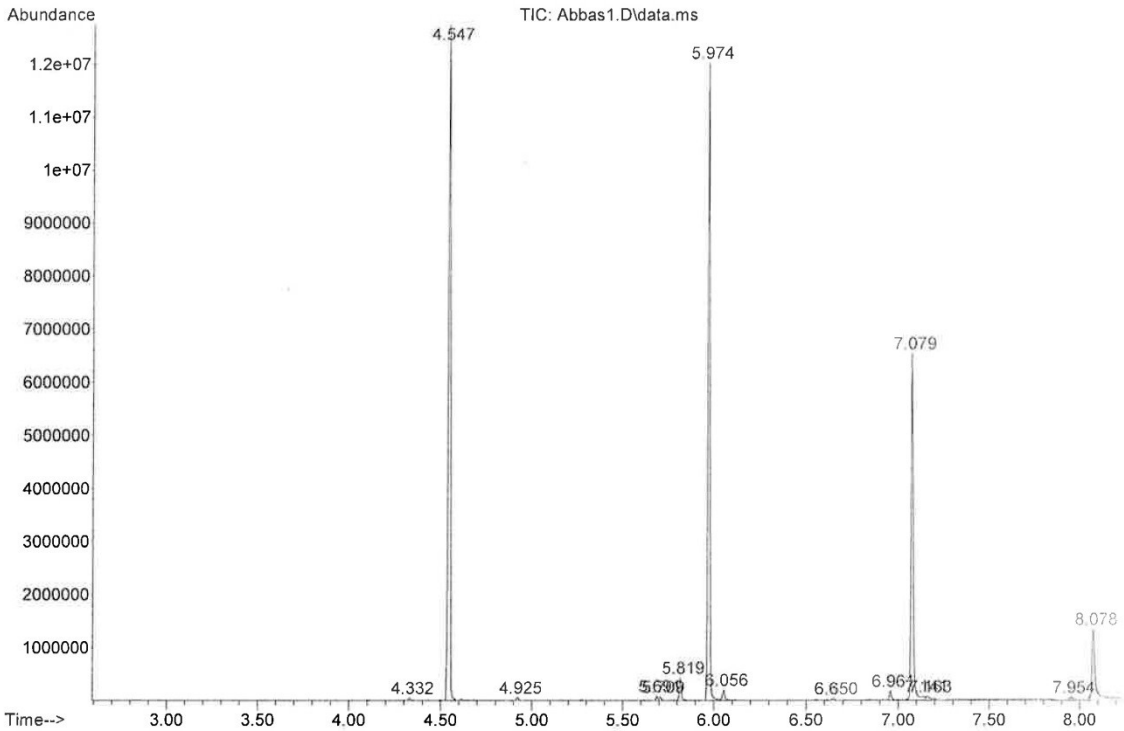



**Fig. S4**. Gas chromatogram of *fraction 2*

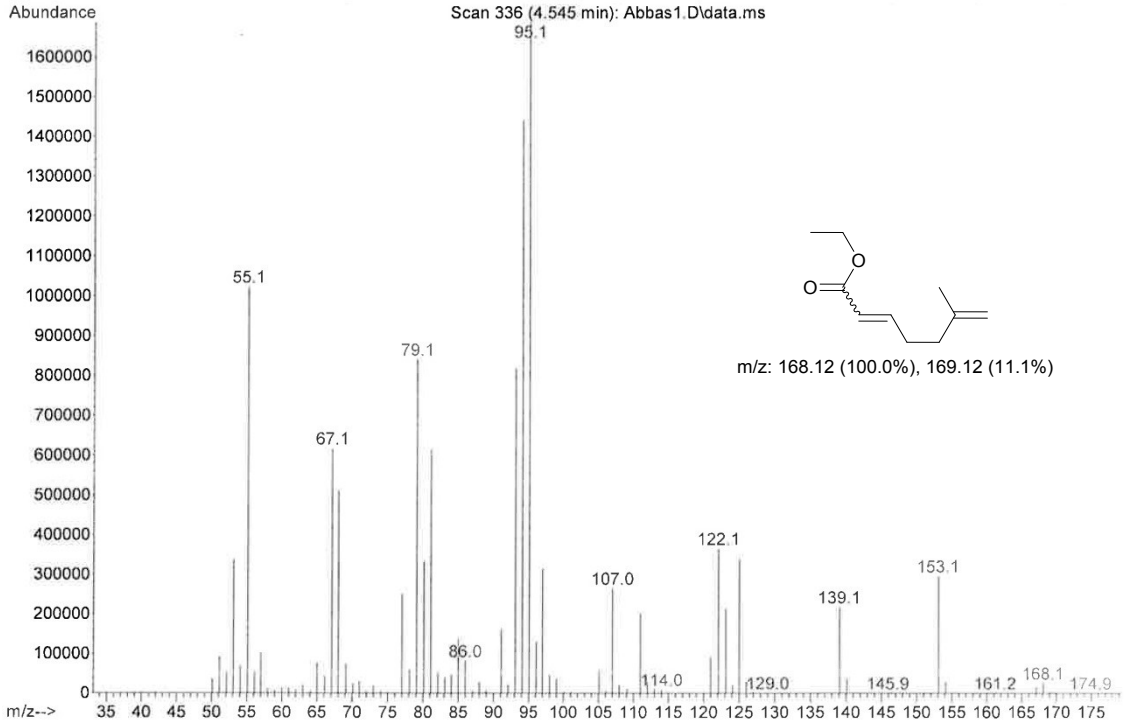



**Fig. S5**. Mass spectrum of the peak at 4.545 min from the gas chromatogram of *fraction 2*

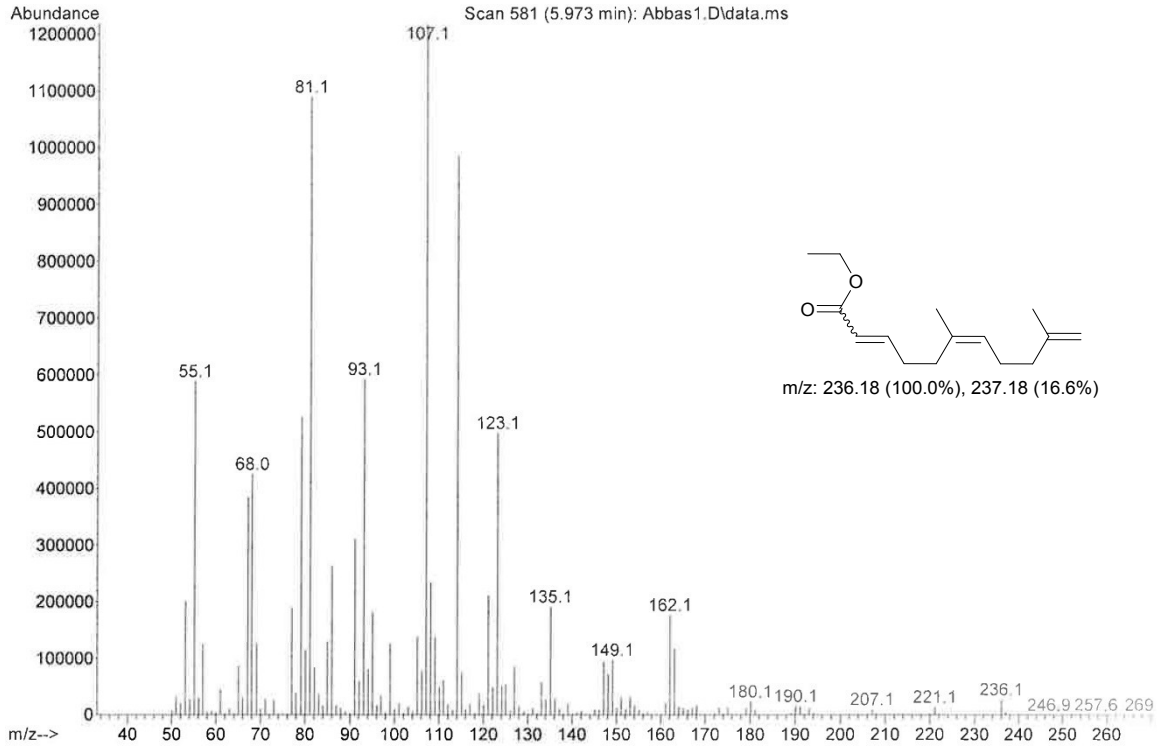



**Fig. S6**. Mass spectrum of the peak at 5.973 min from the gas chromatogram of *fraction 2*

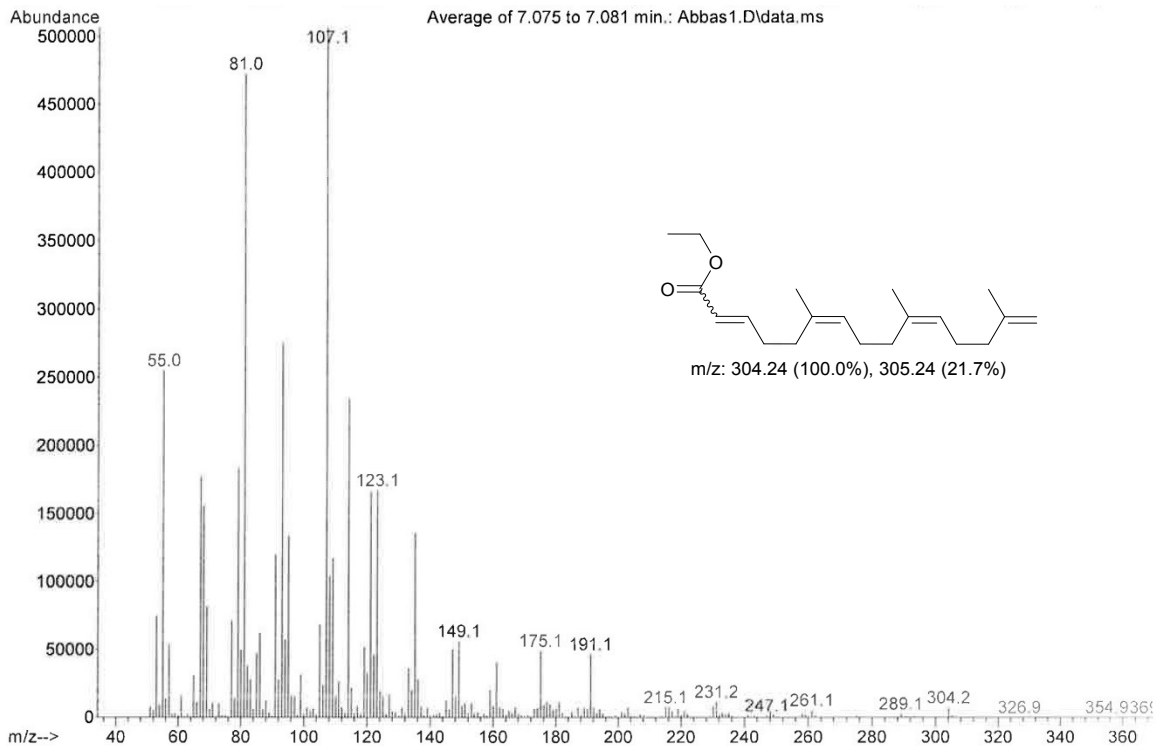



**Fig. S7**. Mass spectrum of the peak at 7.081 min from the gas chromatogram of *fraction 2*

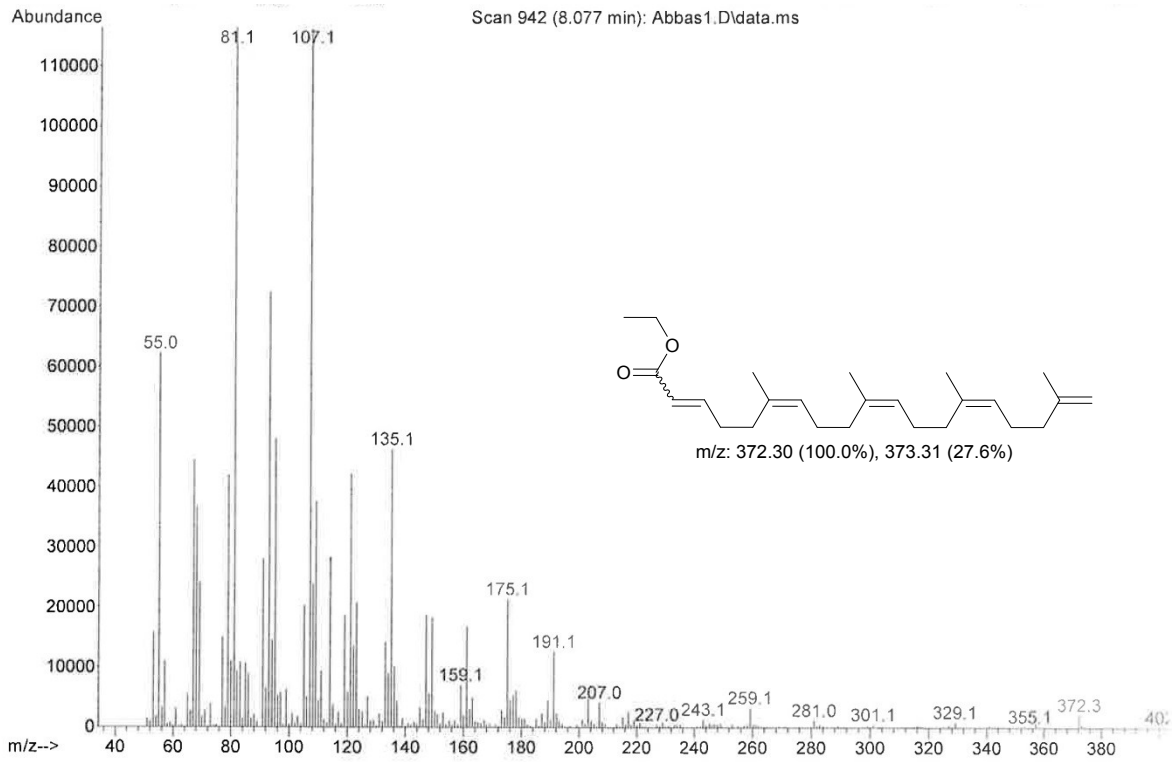



**Fig. S8**. Mass spectrum of the peak at 4.545 min from the gas chromatogram of *fraction 2*

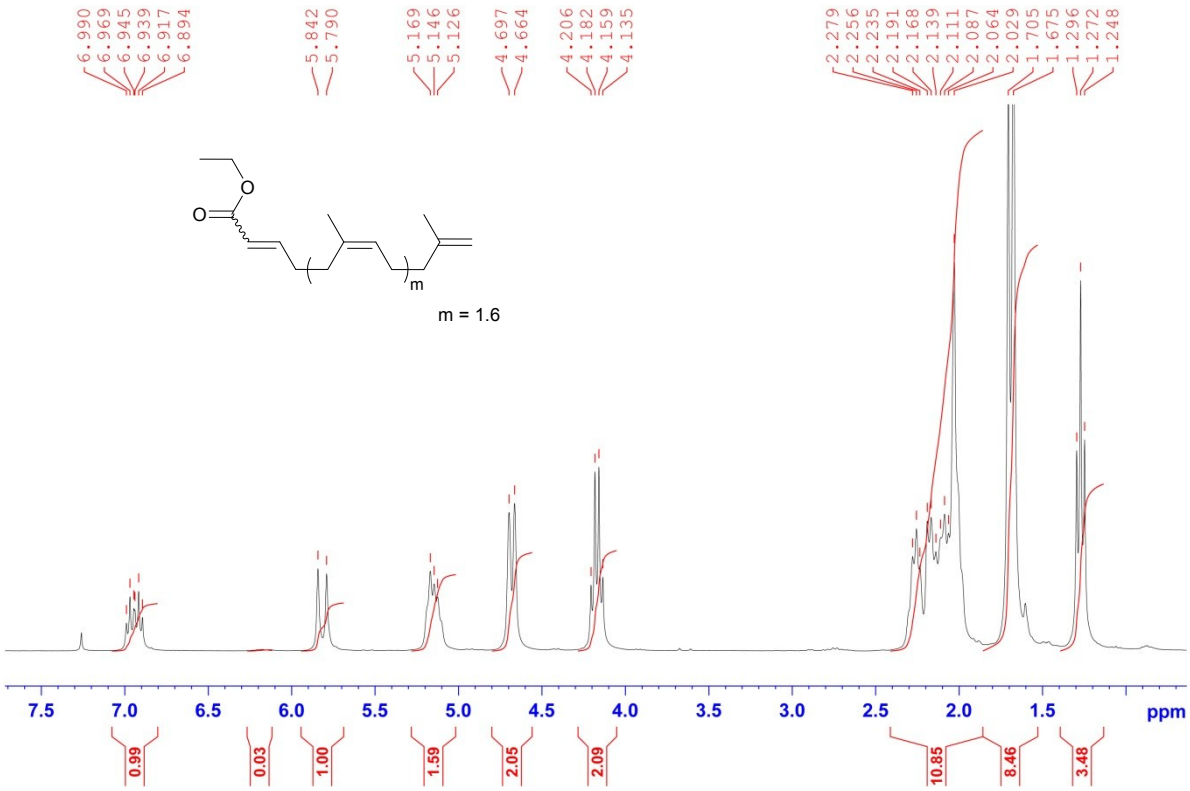



**Fig. S9**. $^{1}$H-NMR of *fraction 2* from the natural rubber degradation experiment

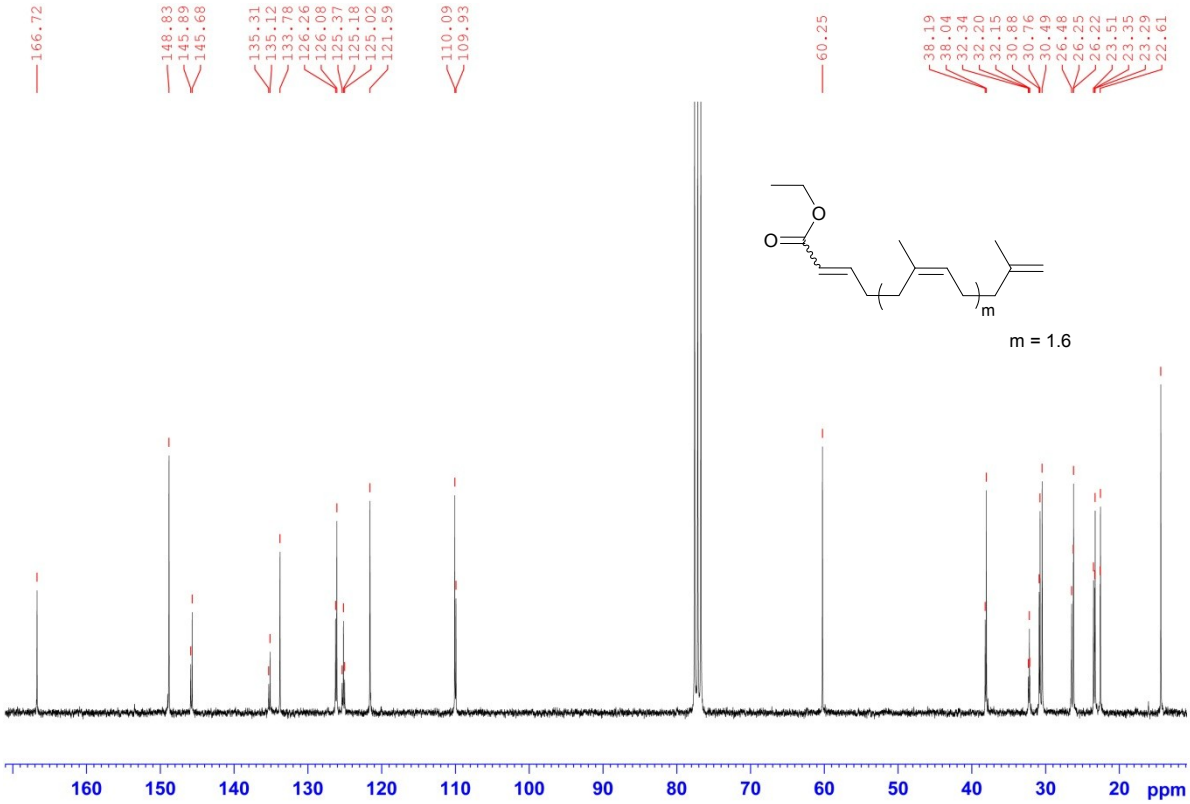



**Fig. S10**. $^{13}$C{$^{1}$H}-NMR of *fraction 2* from the natural rubber degradation experiment

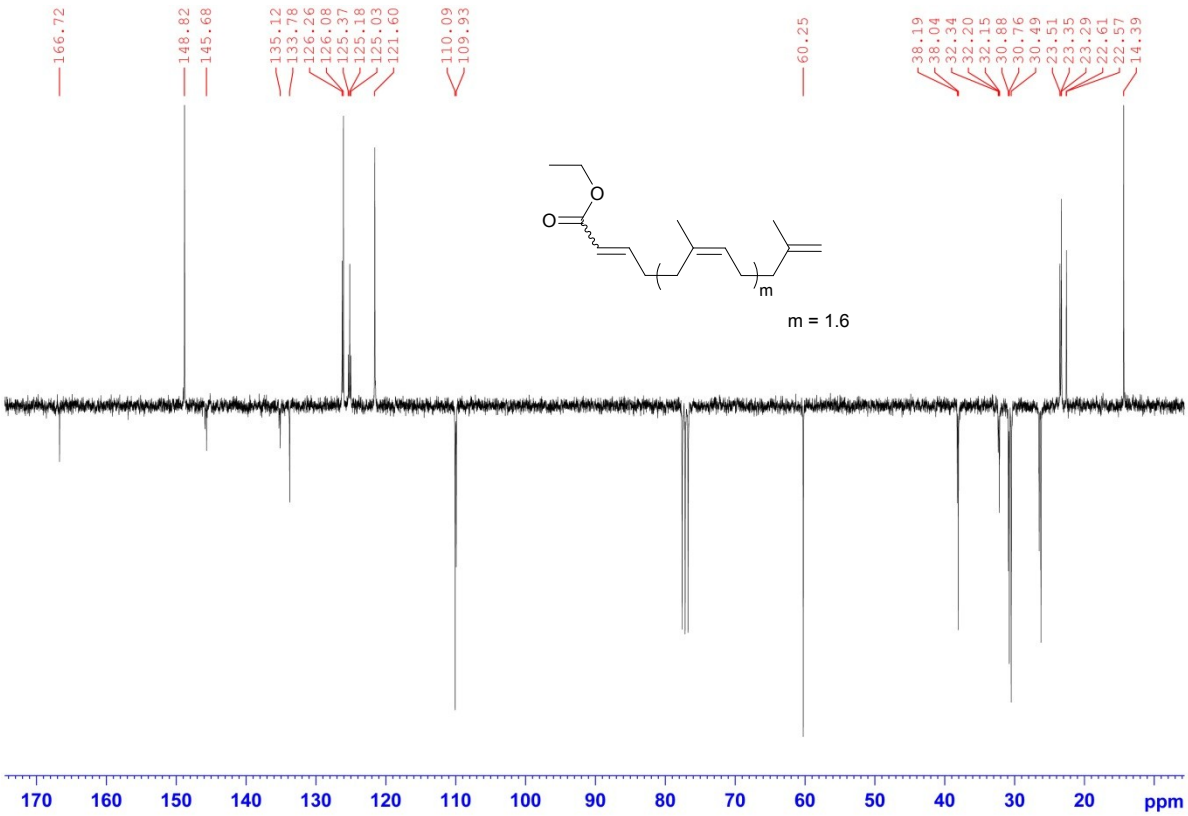



**Fig. S11**. APT-$^{13}C\{^{1}H\}$--NMR of *fraction 2* from the natural rubber degradation experiment

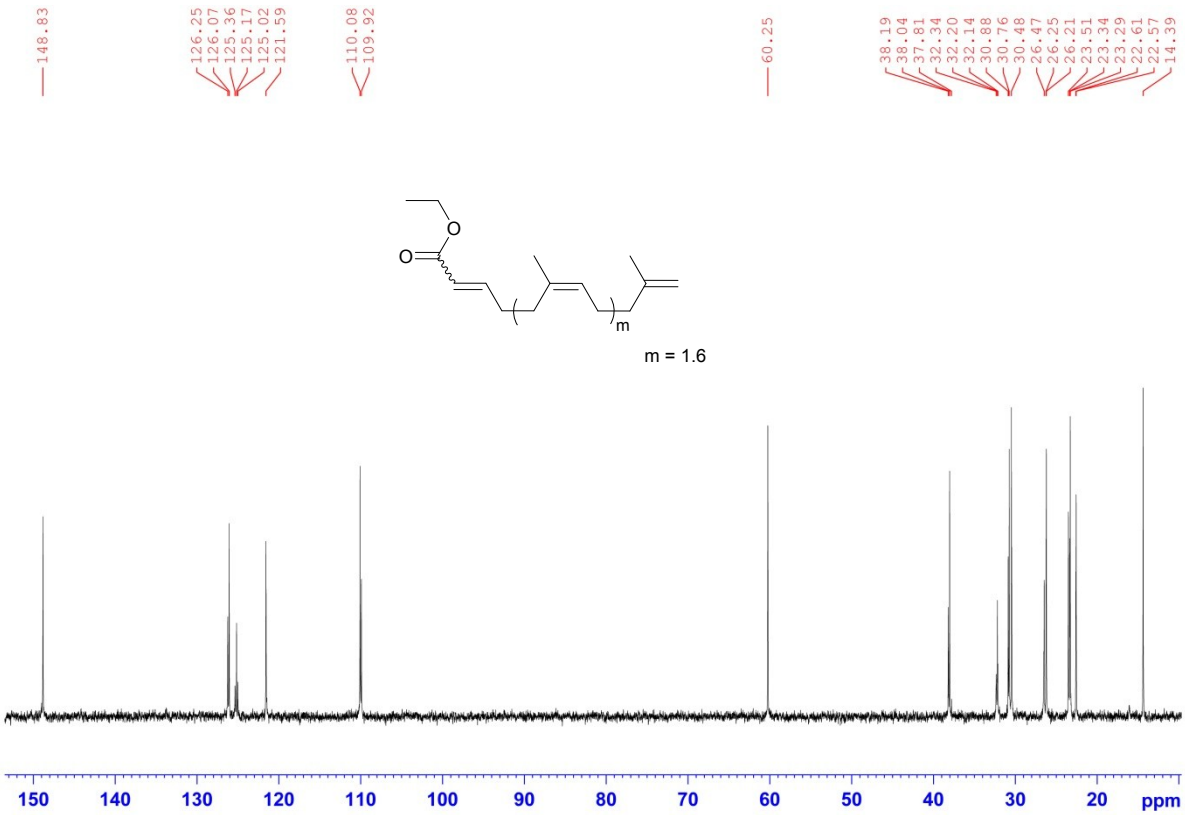



**Fig. S12**. DEPT-45 of *fraction 2* from the natural rubber degradation experiment

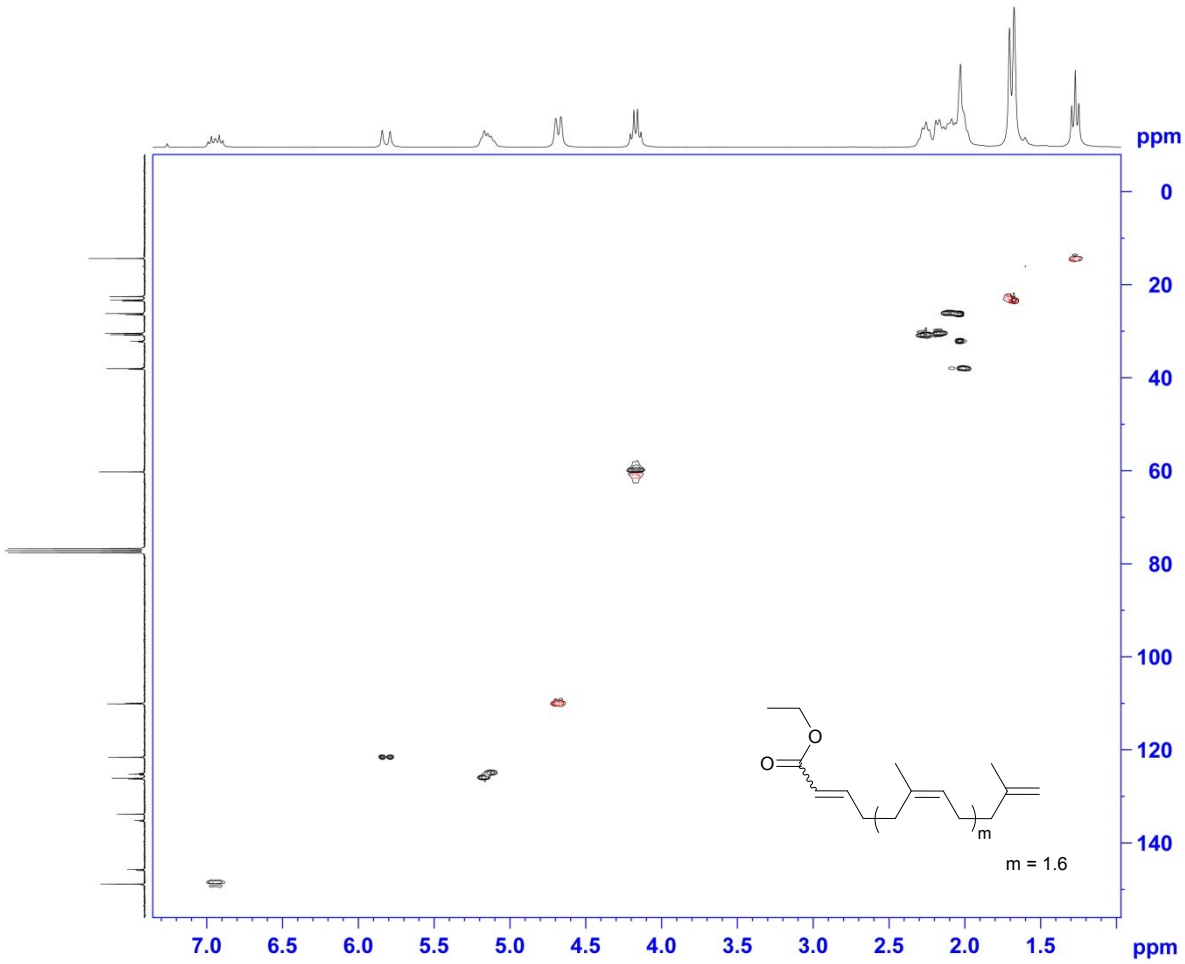



**Fig. S13**. $^{1}$H-$^{13}$C-HSQC of *fraction 2* from the natural rubber degradation experiment

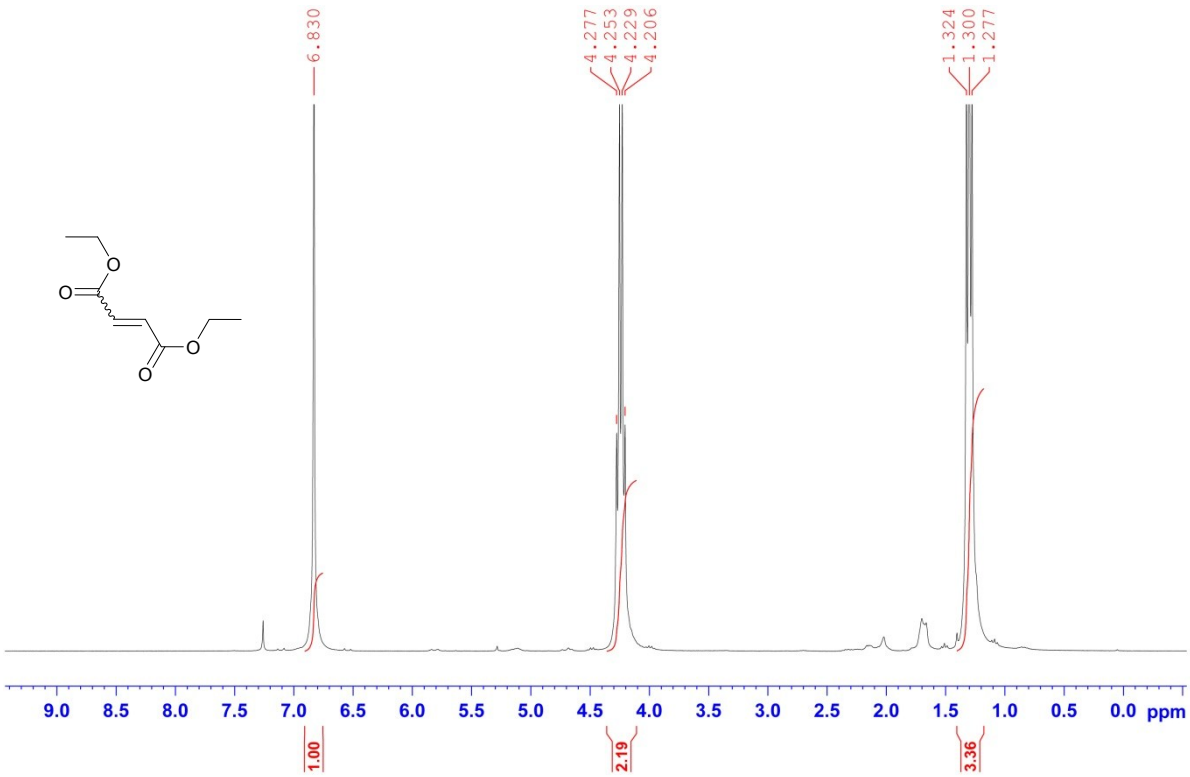



**Fig. S14**. $^{1}$H-NMR of *fraction 3* from the natural rubber degradation experiment

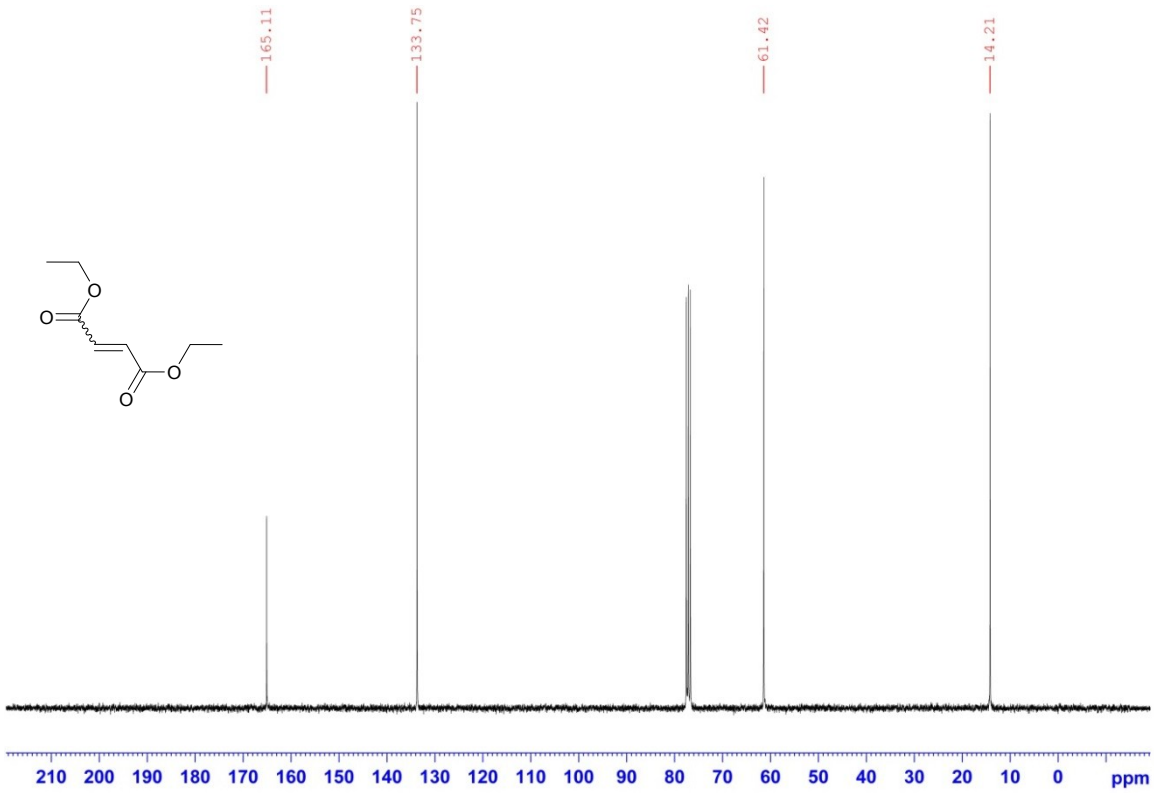
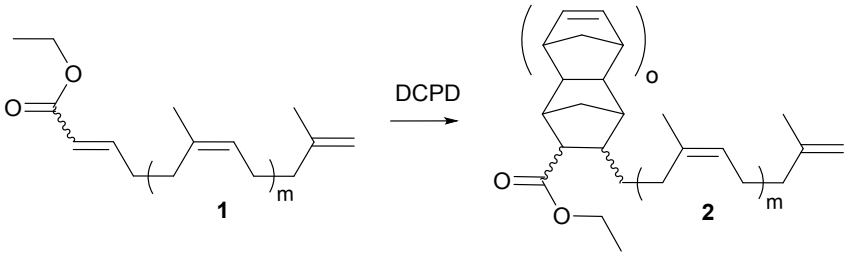



**Fig. S15**. $^{13}C\{^1H\}$-NMR of *fraction 3* from the natural rubber degradation experiment

**Reaction of the oligoenoates 1 with dicyclopentadiene**




A mixture of **1** (m= 3.4; 499.3 mg; 1.25 mmol) and DCPD (1002 mg; 7.6 mmol) was reacted at 200°C for 1 h in a Monowave reactor (Anton Paar). Upon cooling to room temperature and removal of volatiles, a brown oil was obtained. Excess DCPD was removed via column chromatography (200 mL silica; eluent: cyclohexane) sampling the spot on the TLC at $R_f$ = 0.95 (cyclohexane). Afterwards the eluent was changed to ethyl acetate and **2** was eluted ($R_f$ of **2** = 0.41-0.35 (cyclohexane : ethyl acetate = 20 : 1)). Yield: 628.4 mg containing 3-7 % unreacted **1**

The content of tetracyclo[6.2.1.1$^{3,6}$.0$^{2,7}$]dodec-9-ene-4-carboxylate derivatives (o = 1) or potentially even higher oligomers was estimated from the $^{13}C$ NMR spectrum (peaks at 136.4, 136.3, 135.7, 135.6 ppm are characteristic for o = 1, 2, etc.) approx. 35 % (i. e. o =0.35).

$^1H$-NMR (δ, $CDCl_3$, 300 MHz): 6.27-5.89 (m, 2H, protons from cyclic double bonds), 5.12 (bs, 3.90H, -C($CH_3$)=C*H*-); 4.70, 4.68 (s, 2.2H, -C($CH_3$)=C$H_2$), 4.23-3.99 (m, 2.4H, COOC$H_2$CH$_3$); 3.16-0.70 (m, 51H, -$CH_2CH_2$-, protons of cyclic aliphatic structures, -C(C$H_3$)=CH-, -C(C$H_3$)=C$H_2$, COOCH$_2$C$H_3$).

$^{13}C\{^1H\}$-NMR (δ, $CDCl_3$, 75 MHz): 176.3-174.4 (-*C*OOEt); 145.9-145.8 (q, -*C*(C$H_3$)=CH$_2$), 138.5-133.7 (-*C*($CH_3$)=CH-, -*C*H=*C*H-), 125.2-124.8 (-C($CH_3$)=*C*H-), 109.9 (-C($CH_3$)=*C*H$_2$), 60.4-60.2 (COO*C*H$_2$CH$_3$), 56.6, 56.2, 53.5, 53.3, 51.6, 50.5, 49.3, 49.2, 47.6-45.2, 43.9, 43.4, 42.5 (aliphatic cyclic carbons), 38.2 (-*C*H$_2$-C($CH_3$)=CH$_2$), 34.7, 34.2, 33.23, 33.20, 32.9, 31.1, 20.9, 30.5, 29.5 (aliphatic cyclic carbons and (-*C*H$_2$CH$_2$-C($CH_3$)=CH-), 26.5 (-*C*H$_2$-C($CH_3$)=CH-), 23.5, 22.6 (-C(*C*H$_3$)=CH-, -C(*C*H$_3$)=CH$_2$), 14.4 (COOCH$_2$*C*H$_3$).

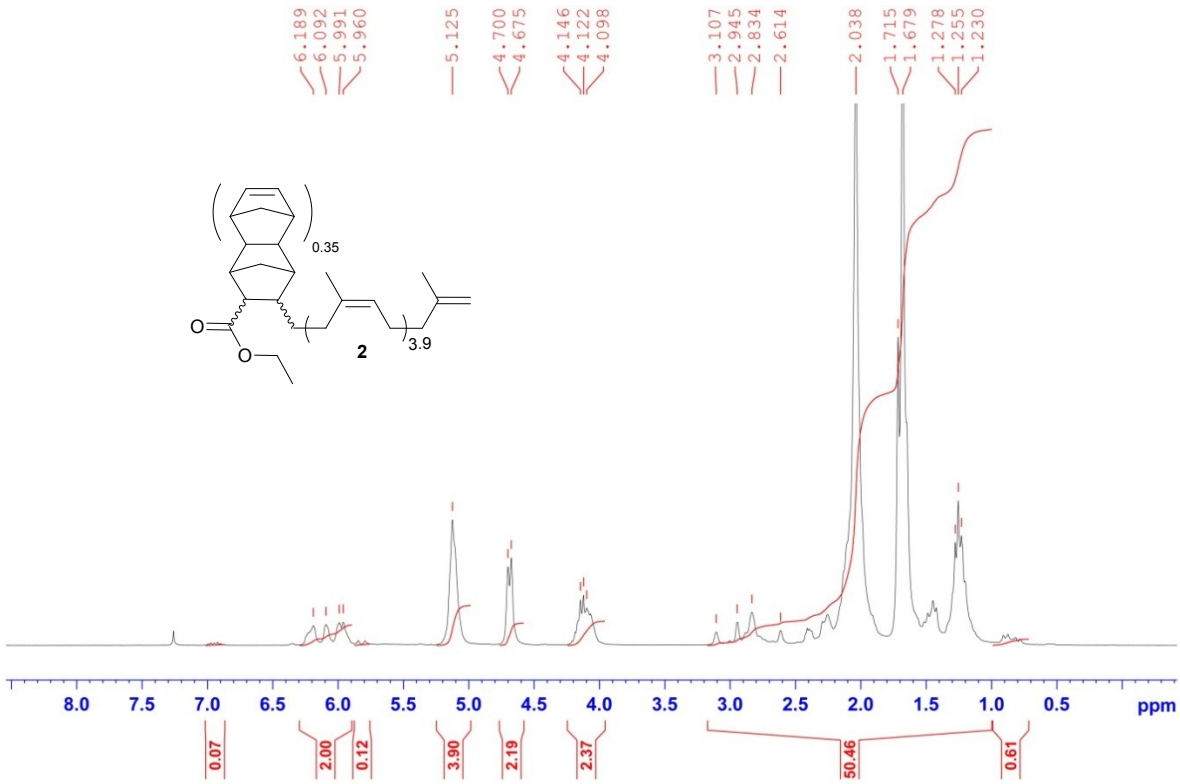



**Fig. S16**. $^{1}$H-NMR of **2**

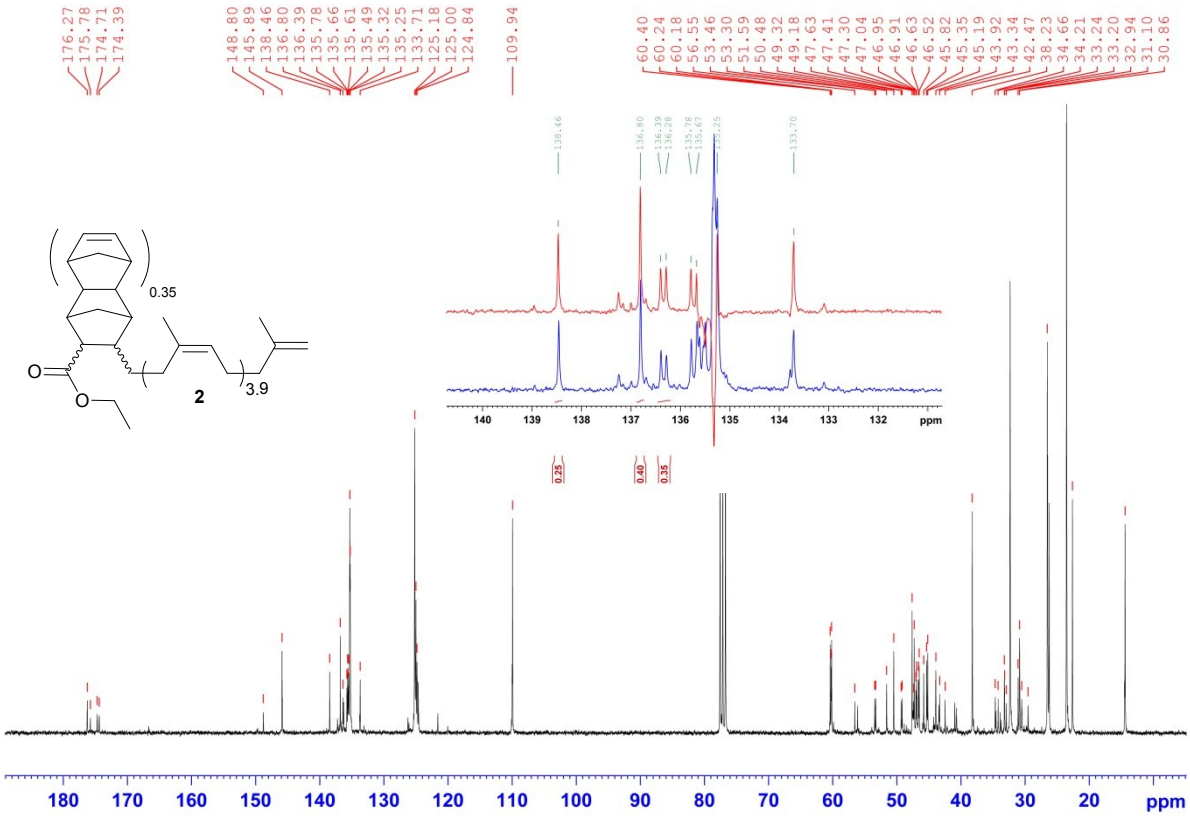



**Fig. S17**. $^{13}$C{$^{1}$H}-NMR of **2**; inset: overlay of the $^{13}$C{$^{1}$H}- and the APT-spectrum of **2** and integration

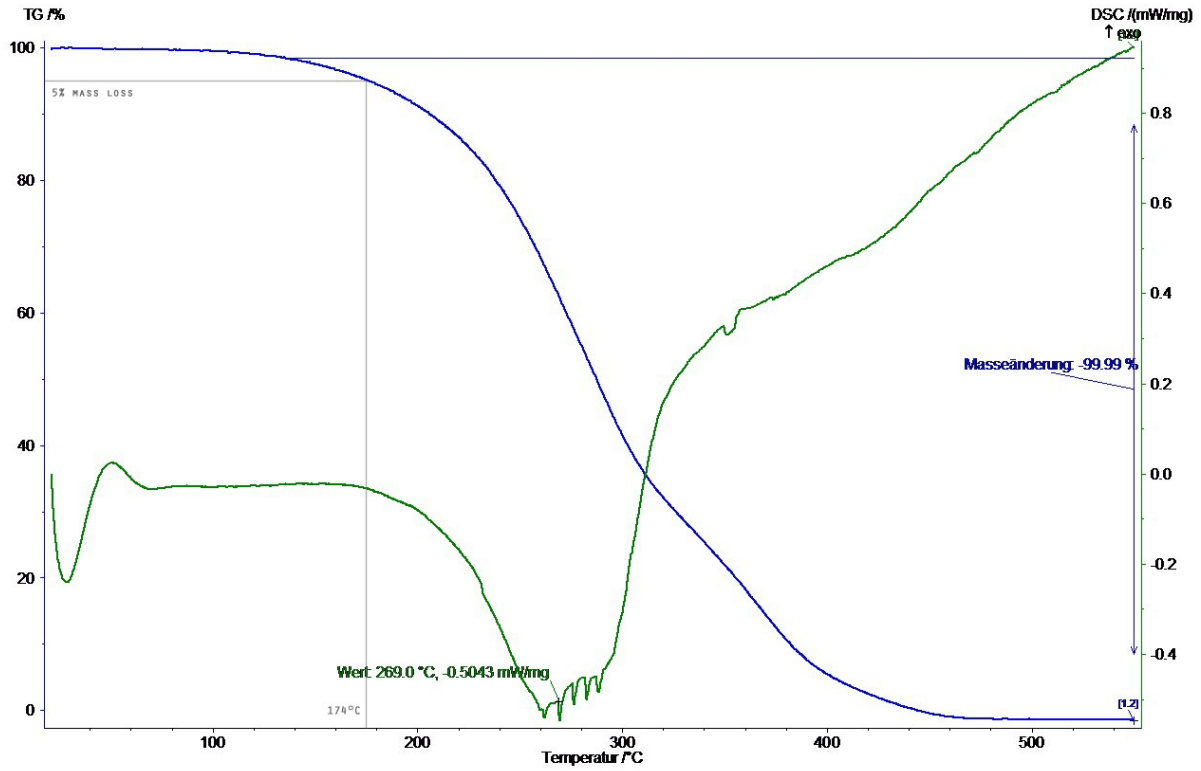
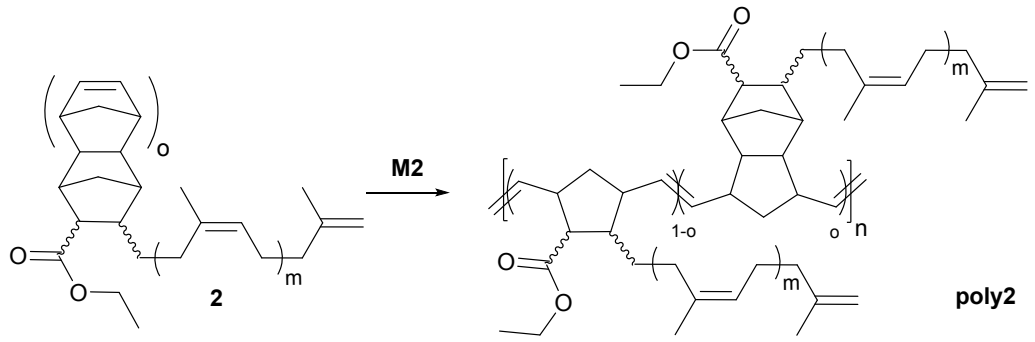



**Fig. S18**. TGA of **2**

**Polymerization of 2**




Monomers **2** (915 mg; m = 3.4, o = 0.35; 2.12 mmol) and a solution of **M2** (0.0024 mmol, **2** : **M2** = 870 : 1) in dichloromethane (100 µL) were combined in a Schlenk-tube and heated until 80°C in a $N_2$-stream. Afterwards the Schlenk-tube was closed and the reaction mixture was stirred for 2 h at 80°C. After cooling the reaction mixture to room temperature, 100 µL of ethyl vinyl ether were added and the reaction mixture was stirred at room temperature for 30 min. The reaction mixture was dropped into ice cold methanol (15 mL) under vigorous stirring. After 15 min without stirring, the supernatant almost color-less methanol-phase was removed and the residual brown liquid phase was dried under vacuum. Yield: 900 mg (98 %). GPC (THF): $M_n$ = 5500; $M_w$ = 40000; PDI = 7.3
Similarly a polymerization with a monomer to initiator of **2** : **M2** = 260 : 1 was conducted, yielding 96% of **poly2**. GPC (THF): $M_n$ = 4500; $M_w$ = 20000; PDI = 4.4
A solution polymerization of **2** (dissolved in 10 mL dichloromethane) with a monomer to initiator of **2** : **M31** = 230 : 1 was conducted, yielding 94% of **poly2**. GPC (THF): $M_n$ = 5000; $M_w$ = 11000; PDI = 2

$^1$H-NMR (δ, $CDCl_3$, 300 MHz): 5.56-5.21 (m, 2H, protons from ring opened double bonds), 5.12 (bs, 3.3H, -C($CH_3$)=C*H*-); 4.68, 4.65 (s, 1.6H, -C($CH_3$)=C$H_2$), 4.26-3.92 (m, 1.9H, COOC$H_2$CH$_3$); 3.25-0.70 (m, 44H, -$CH_2CH_2$-, protons of cyclic aliphatic structures, -C(C$H_3$)=CH-, -C(C$H_3$)=C$H_2$, COOCH$_2$C$H_3$).

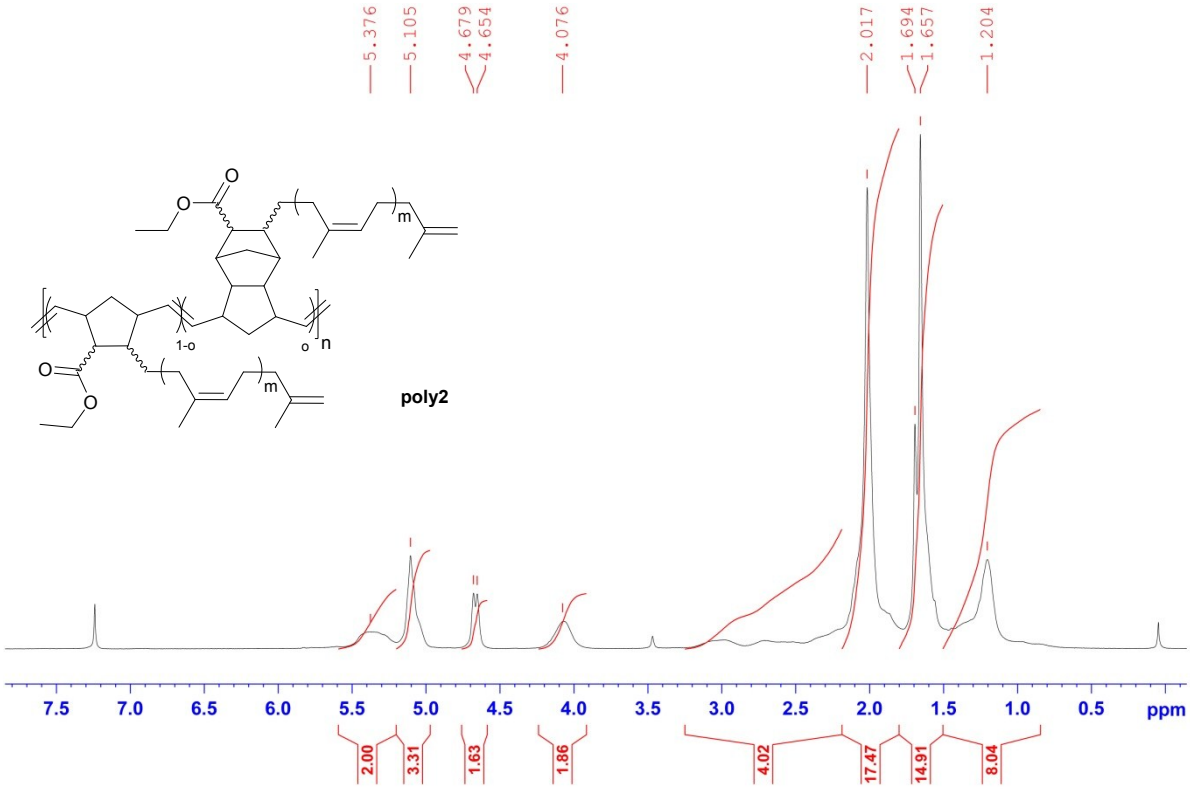



**Fig. S19**. $^1$H-NMR of **poly2**

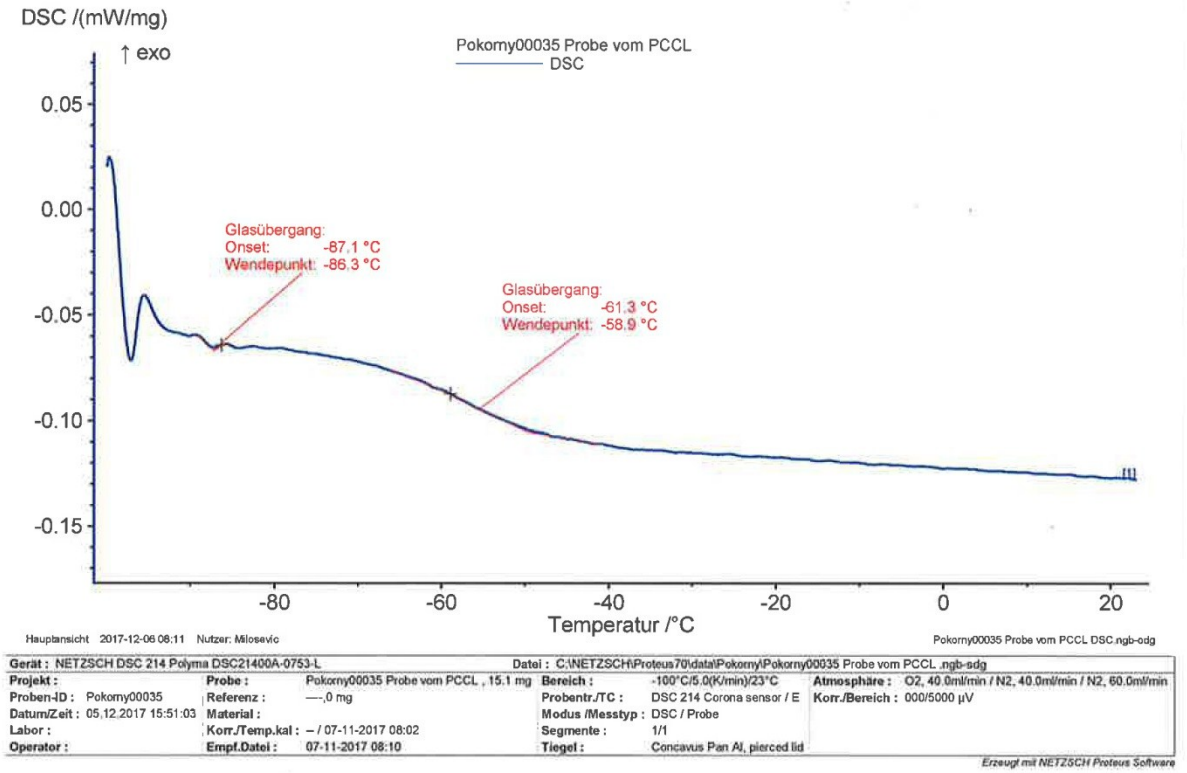



**Fig. S20**. DSC of **poly2** (from **poly2** prepared with **2** : **M2** = 260 : 1)

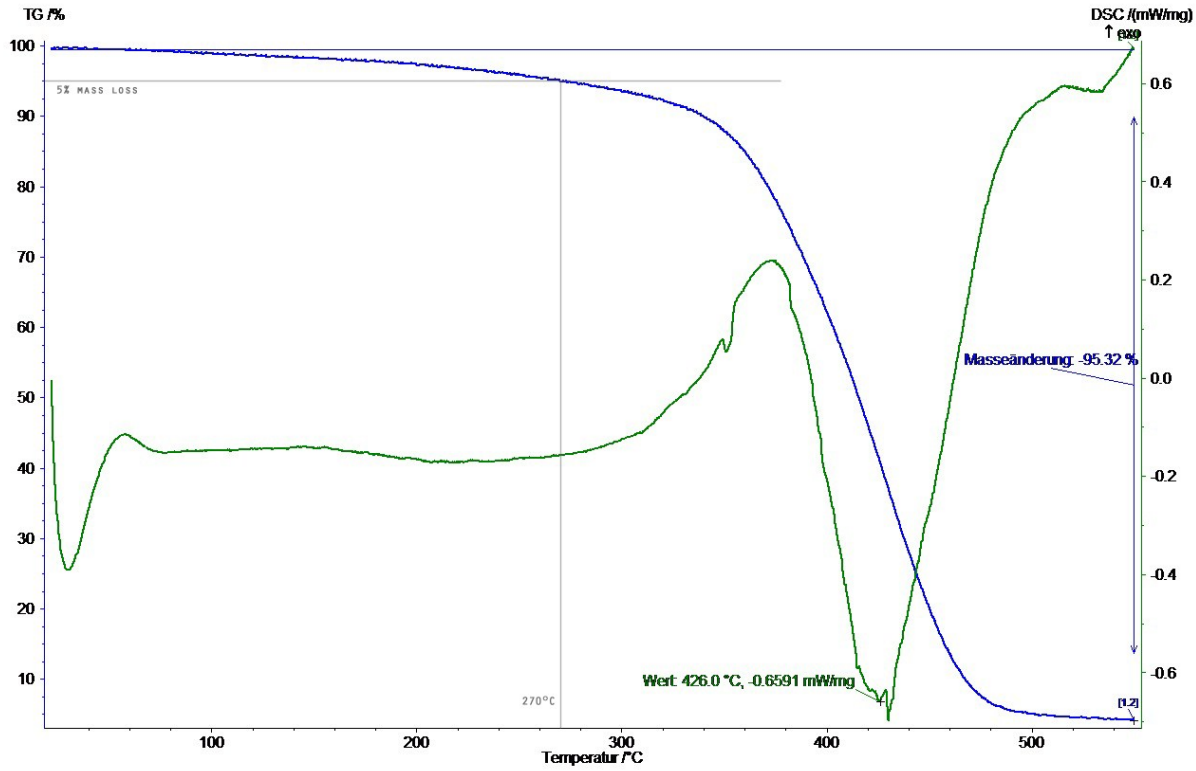



**Fig. S21**. TGA of **poly2**

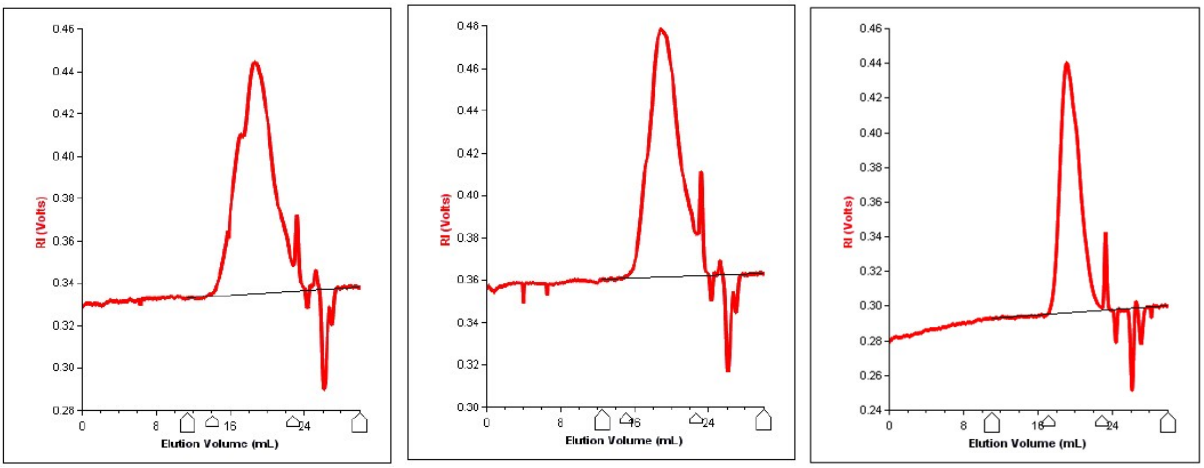



**Fig. S22**. GPC of **poly2**; prepared with the following monomer to initiator ratios, left: **2** : **M2** = 870 : 1; middle: **2** : **M2** = 260 : 1; right: **2** : **M31** = 260 : 1.

## References

[1] a) Fei, J.; Wang, Z.; Cai, Z.; Sun, H.; Cheng, X. *Adv. Synth. Catal.* **2015**, *357*, 4063–4068. DOI: 10.1002/adsc.201500646; b) Barluenga, J.; Lonzi, G.; Tomás, M.; López, L. A. *Chem. Eur. J.* **2013**, *19*: 1573–1576. DOI: 10.1002/chem.201203217; c) Morgan, J. P.; Morrill, C.; Grubbs, R. H. *Org. Lett.* **2002**, *4*, 67–70. DOI: 10.1021/ol016918s