Electronic Supplementary Material (ESI) for Green Chemistry

# Supporting Information

# On the ethenolysis of end-of-life tire granulate

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General Experimental. All chemicals were purchased as reagent grade from commercial suppliers and used without further purification unless otherwise noted. Solvents were dried by passing over $Al_2O_3$ and/or by storing over molecular sieves unless otherwise noted. Column chromatography was performed using silica gel 60 (0.063–0.20 mesh ASTM) or with flash gel (15 - 40 µm). TLC was performed by using Fluka silica gel 60 F254 (0.2 mm) on alumina plates. NMR spectra were recorded on Bruker DRX500 and Bruker DRX300. The chemical shifts ($\delta$) are given in ppm relative to TMS (0 ppm) or to the respective solvent signals, coupling constants are ($J$) in Hz. MS spectra were recorded on a Finnigan MAT95 spectrometer. Rubber granulate (particle size: 0-0.5, 0.5-1.5, 1.5-3 mm) was obtained from *Rubber Technology Weidmann*, Bayreuth, Germany. Sulfur content of tyre rubber granulate and ethenolysis-products was determined ICP-OES (Perkin Elmer Optical Emission Spectrometer „Optima 2000 DV“, Meinhard Nebulizer TR 50-C1, WL = 181.975 and 180.669 nm). HPLC were measured on Hitachi LaPrep Sigma and LaChrom Elite systems. IR spectra were measured on Nicolet 6700 ATR FT-IR Spectrometer (source: ever-glo (9.600 – 20 $cm^{-1}$), beamsplitter: KBr, detector: DTGS CsI). Ethenolysis reactions were carried out in a 250 ml Büchi miniclave steel reactor. For safety reasons the ethene cylinders were connected only before or in the initial stage of the reaction to adjust pressure in the reactor, then they were separated. A large reactor volume allows maintaining constant ethene pressure throughout the reaction.

*General procedure for the ethenolysis of ELT granulate (screening of reaction conditions).* Rubber granulate (500 mg) was placed in a 250 mL Büchi miniclave and the respective amount of toluene (8 – 150 ml) was added with stirring. To this mixture was added the respective catalyst complex (0.0074 – 0.074 mmol/g ELT granulate). The reactor was closed and degassed by three freeze-and-thaw cycles to replace all other gases by ethene. The ethene pressure in the reactor was adjusted to 7 bar and the reactor heated to the respective reaction temperature for the designated reaction time. After completion of the reaction the reactor was allowed to cool to rt and the reaction mixture was centrifuged (10 minutes, 5000 rpm) or filtered over a short plug of silica using toluene as eluent. The solution was evaporated to obtain oligoisoprenes. The degree of polymerization was determined by $^1H$ NMR spectroscopy.

*Ethenolysis of organic solubles*. 1.8 g of the organic soluble and 50 mL toluene were placed in a 250 mL Büchi miniclave. To the stirred mixture was added catalyst complex 1 (0.03 $mmol/g_{tirerubber}$). The reactor was closed and argon and some air removed by three freeze-and-thaw cycles and replaced with ethene. The ethene pressure in the reactor was adjusted to 7 bar and the reactor heated to 80°C for 20 hours. Then the reactor was allowed to cool to rt and the reaction mixture was filtered over a short plug of silica using toluene as the eluent. The combined solutions were evaporated, to obtain a mixture primarily composed of oligoisoprenes. Yield: 1.8 g of oligoisoprenes, average dp = 6.3.

*Determination of the average degree of polymerization*. The average size of the oligoisoprenes was determined via $^1$H NMR spectroscopy by comparing the resonance ratios of the internal olefinic protons ($\delta$ = 5.1 ppm) to the $\beta$-proton of the terminal $–CH=CH_2$-group ($\delta$ = 5.8 ppm). In addition, the resonance ratios of the internal methyl-protons ($\delta$ = 1.68 ppm) proportional to the $\beta$–methyl group at the terminal olefin ($\delta$ = 1.72 ppm) were calculated.

## NMR spectra of ethenolysis mixtures

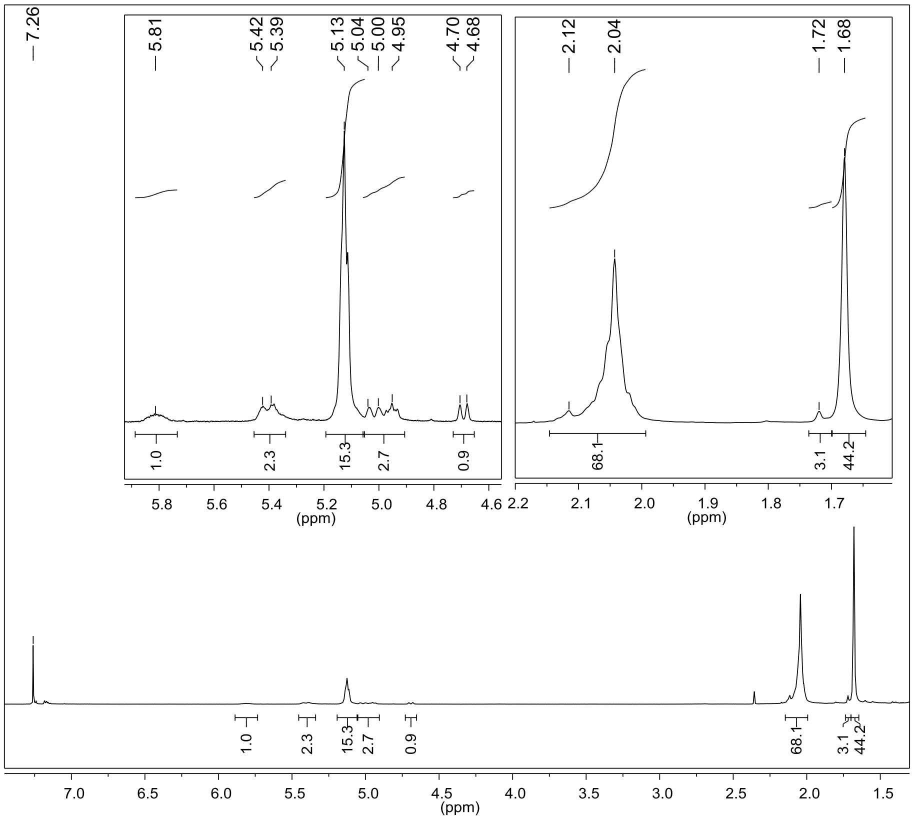
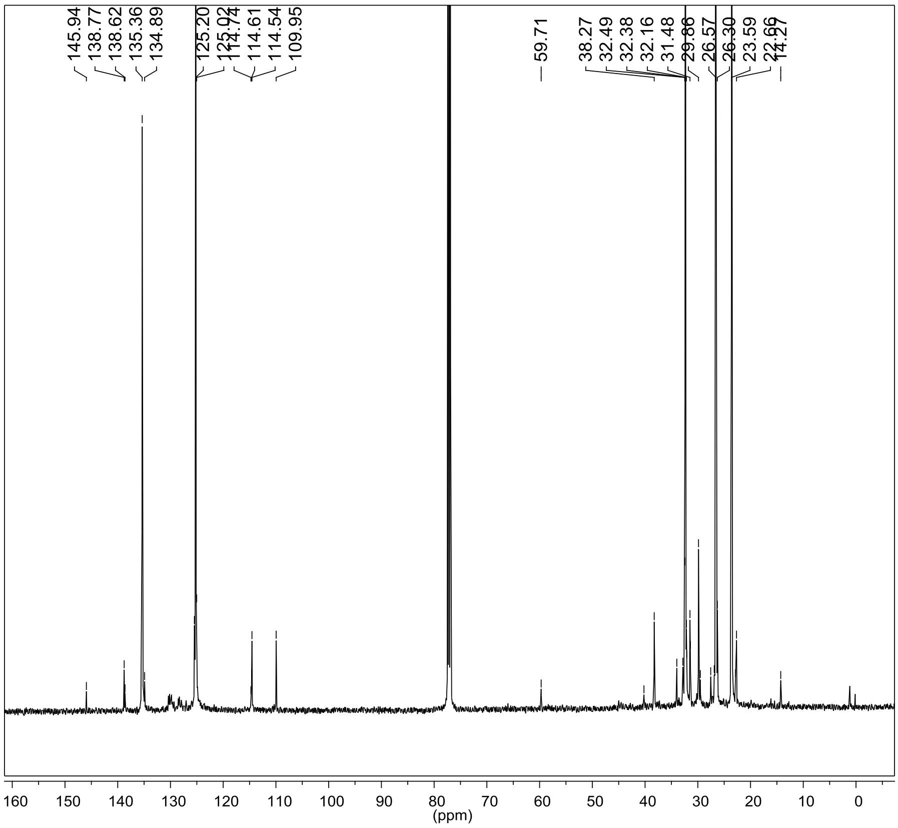
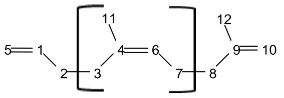


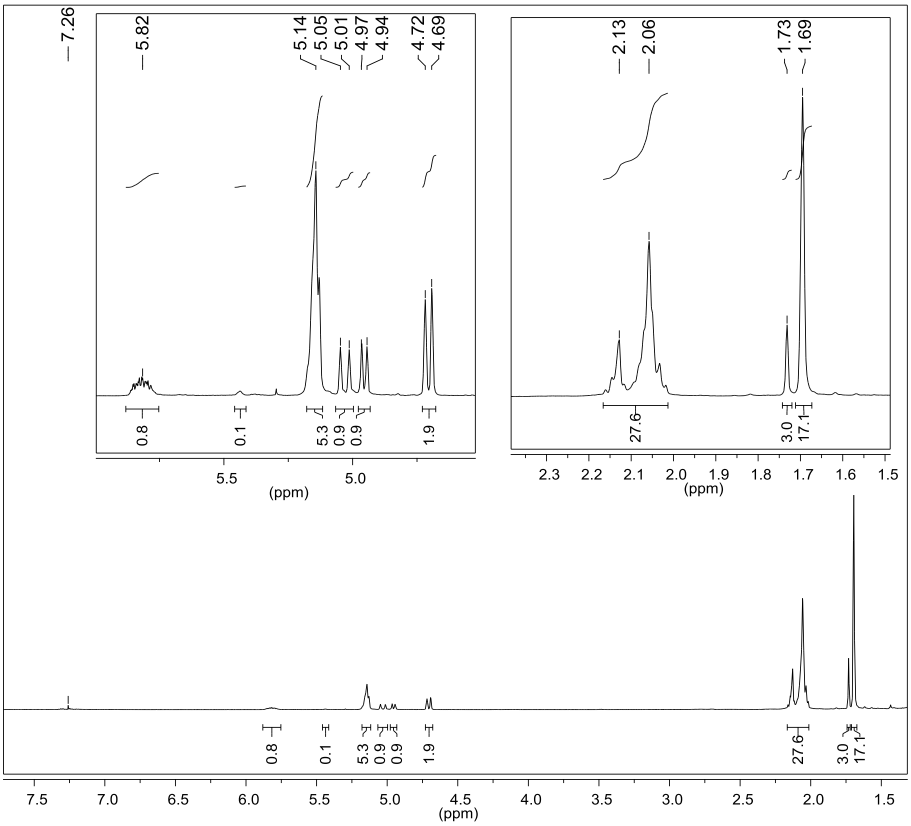
Figure S1: $^{1}$H NMR spectrum of oligoisoprene-mixture obtained from 1 ethenolysis step.





| | Parameter | Value |
|---|---|---|
| 1 | Title | feb01av |
| 2 | Comment | Wolf 540 |
| 3 | Origin | Bruker BioSpin GmbH |
| 4 | Solvent | CDCl3 |
| 5 | Temperature | 300.0 |
| 6 | Pulse Sequence | zgpg30 |
| 7 | Number of Scans | 5000 |
| 8 | Receiver Gain | 7298 |
| 9 | Relaxation Delay | 0.4000 |
| 10 | Pulse Width | 7.4000 |
| 11 | Acquisition Time | 0.8848 |
| 12 | Acquisition Date | 2012-02-01T23:53:00 |
| 13 | Spectrometer Frequency | 125.77 |
| 14 | Spectral Width | 37037.0 |
| 15 | Lowest Frequency | -5923.5 |
| 16 | Nucleus | 13C |
| 17 | Acquired Size | 32768 |
| 18 | Spectral Size | 65536 |

Figure S2: $^{13}$C NMR spectrum of oligoisoprene-mixture obtained from ethenolysis.



example 2nd ethenolysis step

| | Parameter | Value |
|---|---|---|
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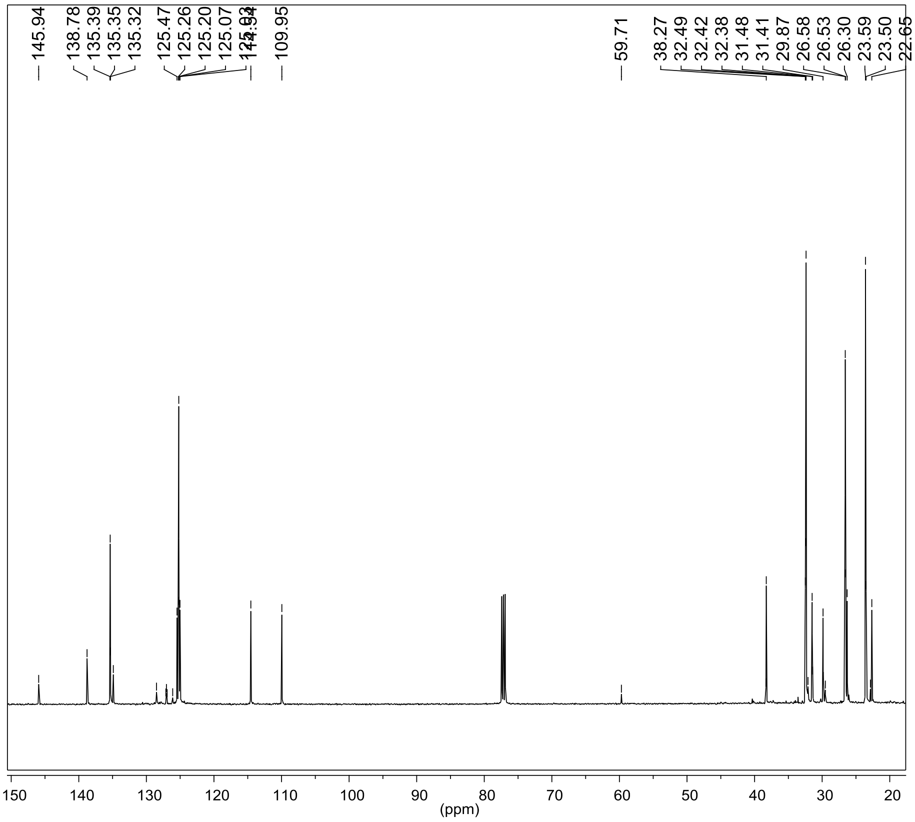
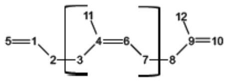
| 2 | Origin | Bruker BioSpin GmbH |
| 3 | Spectrometer | spect |
| 4 | Solvent | CDCl3 |
| 5 | Temperature | 300.0 |
| 6 | Pulse Sequence | zg30 |
| 7 | Number of Scans | 80 |
| 8 | Receiver Gain | 40 |
| 9 | Relaxation Delay | 0.5000 |
| 10 | Pulse Width | 11.1000 |
| 11 | Acquisition Time | 3.1720 |
| 12 | Spectrometer Frequency | 500.13 |
| 13 | Spectral Width | 10330.6 |
| 14 | Lowest Frequency | -2090.3 |
| 15 | Nucleus | 1H |
| 16 | Acquired Size | 32768 |
| 17 | Spectral Size | 65536 |

Figure S3: $^{1}$H NMR spectrum of oligoisoprene-mixture obtained from second ethenolysis.

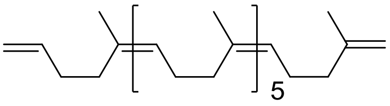




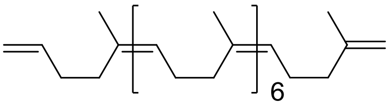
| | Parameter | Value |
|---|---|---|
| 1 | Comment | Wolf 539 |
| 2 | Origin | Bruker BioSpin GmbH |
| 3 | Spectrometer | spect |
| 4 | Solvent | CDCl3 |
| 5 | Temperature | 300.0 |
| 6 | Pulse Sequence | zgpg30 |
| 7 | Number of Scans | 5000 |
| 8 | Receiver Gain | 14596 |
| 9 | Relaxation Delay | 0.4000 |
| 10 | Pulse Width | 7.4000 |
| 11 | Acquisition Time | 0.8848 |
| 12 | Spectrometer Frequency | 125.77 |
| 13 | Spectral Width | 37037.0 |
| 14 | Lowest Frequency | -5923.5 |
| 15 | Nucleus | 13C |
| 16 | Acquired Size | 32768 |
| 17 | Spectral Size | 65536 |

Figure S4: $^{13}$C NMR spectrum of oligoisoprene-mixture obtained from second ethenolysis.

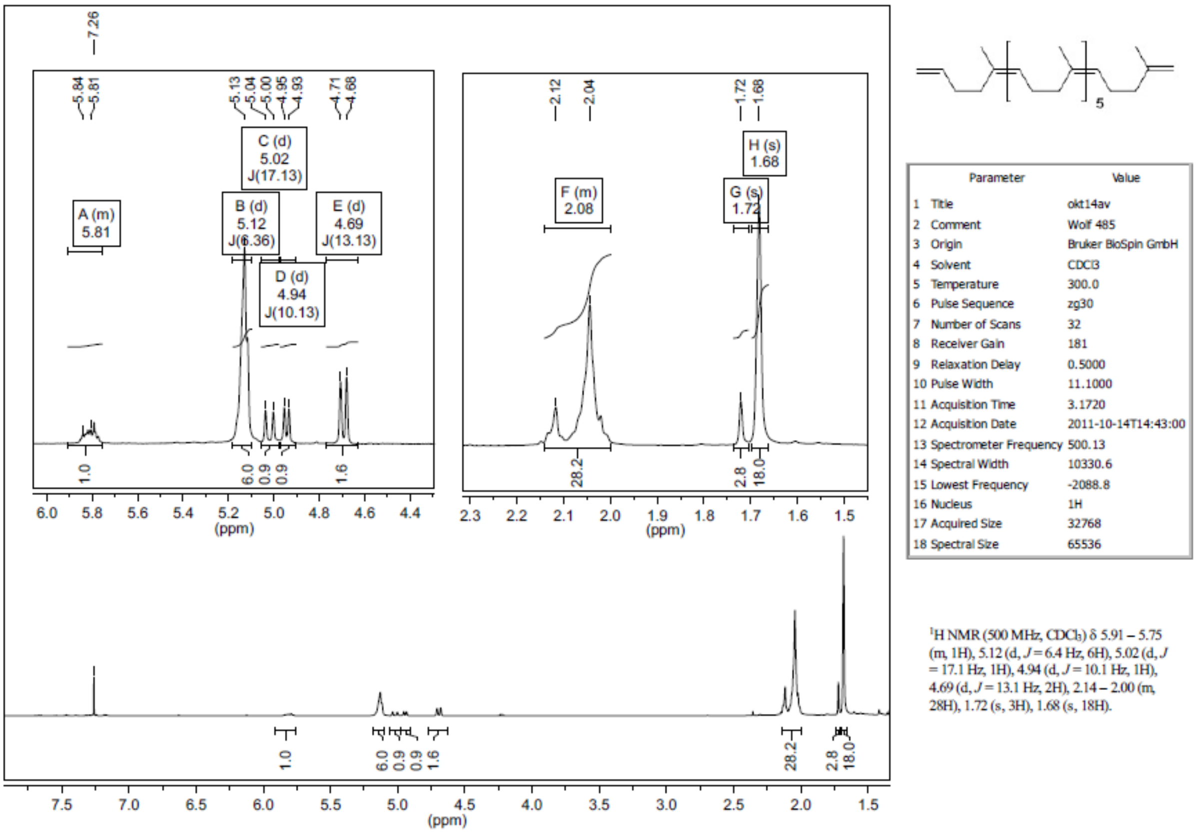
$^{1}$H-NMR spectroscopic data of isolated and previously unknown heptameric and octameric isoprenes



$^{1}$H NMR (500 MHz, $CDCl_3$) δ 5.91 – 5.75 (m, 1H), 5.12 (d, *J* = 6.4 Hz, 6H), 5.02 (d, *J* = 17.1 Hz, 1H), 4.94 (d, *J* = 10.1 Hz, 1H), 4.69 (d, *J* = 13.1 Hz, 2H), 2.14 – 2.00 (m, 28H), 1.72 (s, 3H), 1.68 (s, 18H).



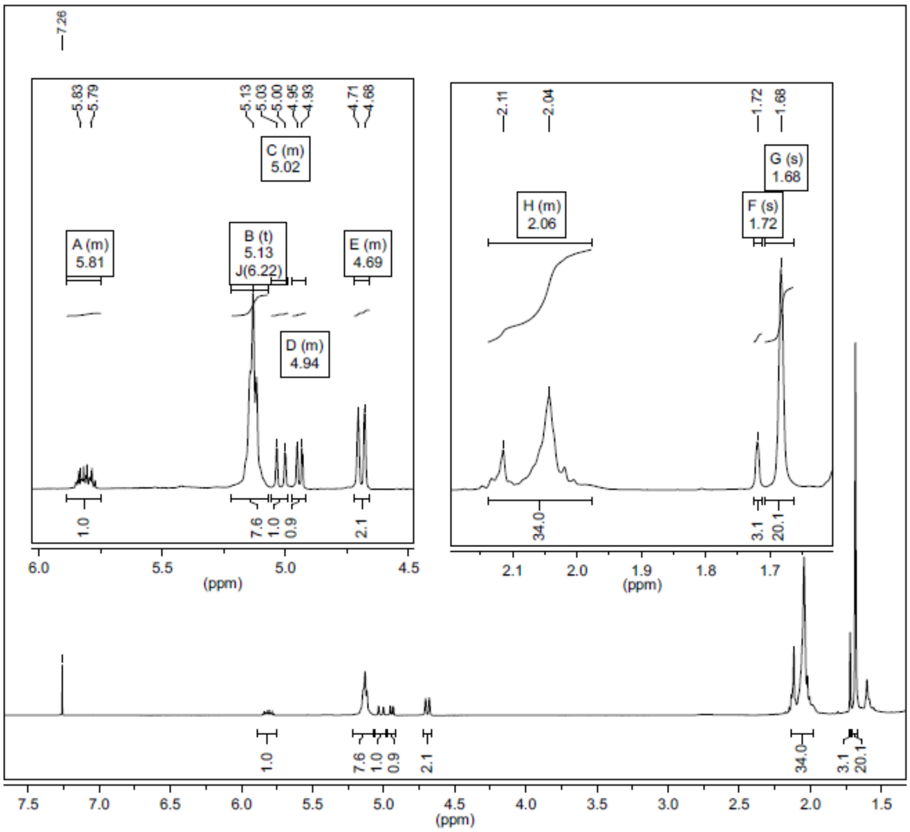
$^{1}$H NMR (500 MHz, $CDCl_3$) δ 5.89 – 5.75 (m, 1H), 5.13 (t, *J* = 6.2 Hz, 7H), 5.06 – 4.99 (m, 1H), 4.97 – 4.92 (m, 1H), 4.72 – 4.66 (m, 2H), 2.14 – 1.98 (m, 32H), 1.72 (s, 3H), 1.68 (s, 21H).

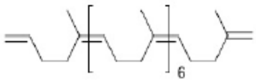


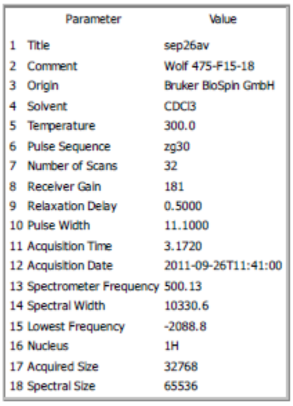
| Parameter | | Value |
|---|---|---|
| 1 | Title | okt14av |
| 2 | Comment | Wolf 485 |
| 3 | Origin | Bruker BioSpin GmbH |
| 4 | Solvent | CDCl3 |
| 5 | Temperature | 300.0 |
| 6 | Pulse Sequence | zg30 |
| 7 | Number of Scans | 32 |
| 8 | Receiver Gain | 181 |
| 9 | Relaxation Delay | 0.5000 |
| 10 | Pulse Width | 11.1000 |
| 11 | Acquisition Time | 3.1720 |
| 12 | Acquisition Date | 2011-10-14T14:43:00 |
| 13 | Spectrometer Frequency | 500.13 |
| 14 | Spectral Width | 10330.6 |
| 15 | Lowest Frequency | -2088.8 |
| 16 | Nucleus | 1H |
| 17 | Acquired Size | 32768 |
| 18 | Spectral Size | 65536 |

$^{1}$H NMR (500 MHz, $CDCl_3$) δ 5.91 – 5.75 (m, 1H), 5.12 (d, *J* = 6.4 Hz, 6H), 5.02 (d, *J* = 17.1 Hz, 1H), 4.94 (d, *J* = 10.1 Hz, 1H), 4.69 (d, *J* = 13.1 Hz, 2H), 2.14 – 2.00 (m, 28H), 1.72 (s, 3H), 1.68 (s, 18H).

Figure S5: $^{1}$H NMR spectrum of oligoisoprene (n = 7).







| | Parameter | Value |
|---|---|---|
| 1 | Title | sep26av |
| 2 | Comment | Wolf 475-F15-18 |
| 3 | Origin | Bruker BioSpin GmbH |
| 4 | Solvent | CDCl3 |
| 5 | Temperature | 300.0 |
| 6 | Pulse Sequence | zg30 |
| 7 | Number of Scans | 32 |
| 8 | Receiver Gain | 181 |
| 9 | Relaxation Delay | 0.5000 |
| 10 | Pulse Width | 11.1000 |
| 11 | Acquisition Time | 3.1720 |
| 12 | Acquisition Date | 2011-09-26T11:41:00 |
| 13 | Spectrometer Frequency | 500.13 |
| 14 | Spectral Width | 10330.6 |
| 15 | Lowest Frequency | -2088.8 |
| 16 | Nucleus | 1H |
| 17 | Acquired Size | 32768 |
| 18 | Spectral Size | 65536 |

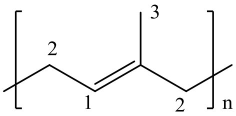
$^1$H NMR (500 MHz, $CDCl_3$) δ 5.89 – 5.75 (m, 1H), 5.13 (t, *J* = 6.2 Hz, 7H), 5.06 – 4.99 (m, 1H), 4.97 – 4.92 (m, 1H), 4.72 – 4.66 (m, 2H), 2.14 – 1.98 (m, 32H), 1.72 (s, 3H), 1.68 (s, 21H).

Figure S6: $^1$H NMR spectrum of oligoisoprene (n = 8).

NMR shifts assignment based on the spectra of natural rubber and isolated monomer and oligomers (data are givenhere to support the assigment of theNMR resonances)

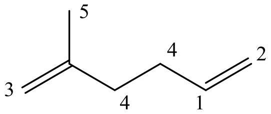
$^1$H-NMR

polyisoprene



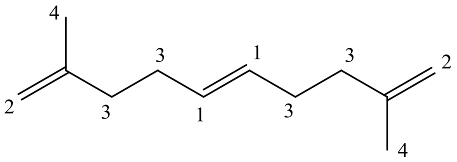
| Proton | shift [ppm] | integral |
|---|---|---|
| 1 | 5.3 | 1 |
| 2 | 2.25 – 2.15 | 4 |
| 3 | 1.8 | 3 |

2-Methyl-1,5-hexadiene



| Proton | shift [ppm] | integral |
|---|---|---|
| 1 | 5.8 – 5.7 | 1 |
| 2 | 5.0 – 4.9 | 2 |
| 3 | 4.8 – 4.7 | 2 |
| 4 | 2.1 – 1.9 | 4 |
| 5 | 1.6 | 3 |

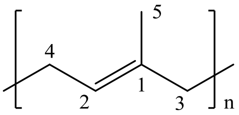
tail-tail-linked isoprene



| Proton | shift [ppm] | integral |
|---|---|---|
| 1 | 5.5 – 5.4 | 2 |
| 2 | 4.8 – 4.7 | 4 |
| 3 | 2.2 – 1.9 | 8 |
| 4 | 1.6 | 6 |

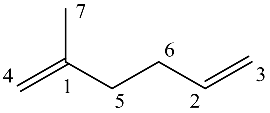
## $^{13}$C-NMR

polyisoprene



| C-Atom | shift [ppm] |
|---|---|
| 1 | 135.4 |
| 2 | 125.2 |
| 3 | 32.4 |
| 4 | 26.6 |
| 5 | 23.6 |

2-methyl-1,5-hexadiene



| C-Atom | shift [ppm] |
|---|---|
| 1 | 145.5 |
| 2 | 138.6 |
| 3 | 114.6 |
| 4 | 110.2 |
| 5 | 37.3 |
| 6 | 32.1 |
| 7 | 22.6 |

Isocratic HPLC trace of organic solubles obtained in the ethenolysis reaction

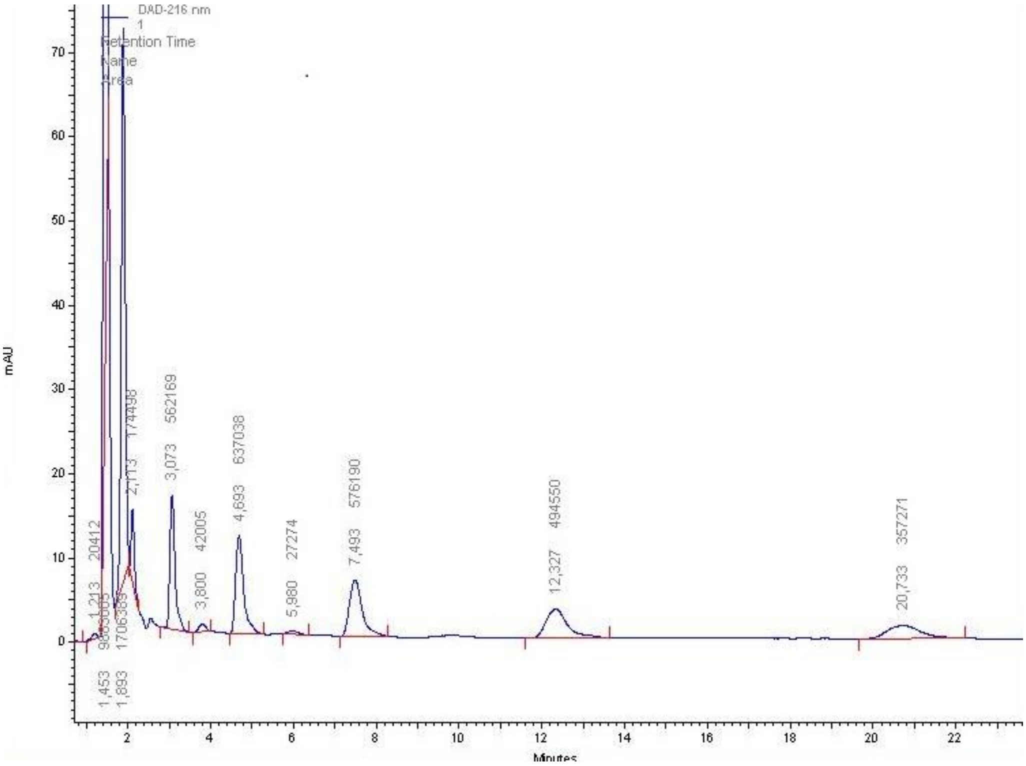


Figure S7. (2.1 min, n=2); (3.1 min, n=3); (4.7 min, n=4); (7.5 min, n= 5); (12.3 min, n= 5); (20.7 min, n= 6) in MeOH: $CH_3CN$ 90: 10.