# Geometric Requirements for Living Anionic Polymerization: Polymerization of rotationally constrained 1,3-Dienes

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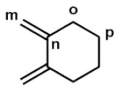
## Supporting Information

### Materials

The solvents cyclohexane (Fisher Science, ≥99.8%) and tetrahydrofuran (THF, Fisher Science, ≥99.8%) were dried over sodium with benzophenone as indicator. 1,2,3,4-Tetrahydro-naphthalene (tetralin, TCI, >97%) was dried with *sec*-butyllithium and 1,1-diphenylethylene (DPE, abcr, 98%) as indicator. The solvents methanol (MeOH, Fisher Science, ≥99.9%), pentane (Fisher Science, ≥99%) and *N,N*-dimethylacetamide (DMAC, Acros Organics, 99.5%) were used as purchased. The chemicals 2-methylcyclohexanone (Acros Organics, 98%), *R*-(-)-carvone (Sigma Aldrich, 98%) dimethyl sulfone (abcr, 99%), potassium *tert*-butoxide (KO$^t$Bu, TCI, >97%) and methyl triphenylphosphonium bromide (Sigma Aldrich, 98%) were used without further purification.
The stabilizer of isoprene (I, Acros Organics, 98%) was removed filtering the monomer through a column containing basic aluminium oxide and purified hereafter by degassing and distillation over calcium hydride (Acros Organics, 93%) and trioctylaluminium (Sigma Aldrich, 25 wt% in hexanes). The synthesized monomers DMCH and IMMCH were purified in analogy to isoprene. *Sec*-Butyllithium (*sec*-BuLi, Acros Organics, 1.3 M in cyclohexane/hexane (92/8)) was used as supplied for reactions on laboratory scale, but diluted in dried cyclohexane for the kinetic investigations of fast polymerization reaction.

### Preparation of 1,2-Dimethylenecyclohexane (DMCH)

The monomer was synthesized in a modified procedure described by Garst *et al.*[1], dissolving the starting material 2-methyl-cyclohexanone (30.3 g, 32.78 mL, 0.27 mmol, 1 eq.) and dimethyl sulfone (58.5 g, 0.62 mmol, 2.3 eq.) in DMAC (377 mL). The solution was heated to 75 °C and subsequently potassium *tert*-butoxide (72.7 g, 0.65 mmol, 2.4 eq.) was added portionwise to avoid a huge temperature increase. After at least 3 hours the reaction was completed (tracked by $^1$H-NMR) and was allowed to cool down to room temperature. Then, the DMAC reaction solution was diluted with water (260 mL) and extracted against pentane (3 times á 180 mL). The combined organic phases were washed with water several times (5-6 times á 100 mL) to remove all DMAC traces. The organic phase was dried over magnesium sulfate and purified by distillation. First, pentane was removed (40 °C, 800 mbar), and then DMCH was fractionated with a Vigreux column (69-70 °C, 120 mbar), yielding a mixture of the three isomers that was enriched in *exo-cis* DMCH (43% yield). The ratio of the isomers can be deduced from NMR measurements (Fig. S5-S10).

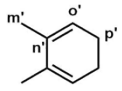


*exo-cis*

***exo-cis:***

$^1$H (400 MHz, C*D*Cl$_3$) δ[ppm] = 4.92 (dt, *J*=2.4, 1.1 Hz, 2H, m), 4.64 (dt, *J*=2.8, 1.5 Hz, 2H, m), 2.25 (m, 4H, o), 1.63 (m, 4H, p).

$^{13}$C (100 MHz, C*D*Cl$_3$) δ[ppm] = 149.83 (2C, N), 107.96 (2C, M), 35.43 (2C, O), 26.92 (2C, P).

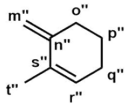


*endo-cis*

***endo-cis:***

$^1$H (400 MHz, C*D*Cl$_3$) δ[ppm] = 5.56 (m, 2H, o'), 2.01 (m, 4H, p'), 1.77 (m, 6H, m').

$^{13}$C (100 MHz, C*D*Cl$_3$) δ[ppm] = 133.83 (2C, N'), 122.04 (2C, O'), 23.01 (2C, P'), 19.79 (2C, M').



*trans*

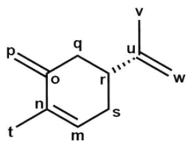
***trans:***

$^1$H (400 MHz, C*D*Cl$_3$) δ[ppm] = 5.68 (m, 1H, r''), 4.86 (s, 1H, m''), 4.74 (s, 1H, m''), 2.59 (s, 1H, q''), 2.35 (ddt, *J*=7.8, 4.4, 1.4 Hz, 2H, o''), 2.12 (m, 2H, p''), 1.81 (m, 3H, t'').

$^{13}$C (101 MHz, C*D*Cl$_3$) δ[ppm] = 144.94 (1C, S''), 132.81 (1C, N''), 123.41 (1C, R''), 107.79 (1C, M''), 32.90 (1C, Q''), 32.52 (1C, O''), 26.53 (1C, P''), 19.38 (1C, T'').

**Preparation of (*5R*)-5-Isopropenyl-2-methyl-1-methylene-2-cyclohexene (IMMCH)**

The monomer was synthesized via a Wittig reaction starting from (*R*)-(–)-carvone. The reaction flask was flame-dried and put under argon atmosphere before distilling the dried THF (170 mL) into the reaction flask. Methyltriphenylphosphonium bromide (27.51 g, 77 mmol, 1.1 eq.) was dissolved in THF and subsequently potassium *tert*-butoxide (8.64 g, 77 mmol, 1.1 eq.) was added to generate the corresponding ylide *in situ*. Afterwards, the carvone (10.52 g, 10.96 mL, 70 mmol, 1.0 eq.) was added via syringe and the reaction mixture was stirred for 14 hours at room temperature. After completion, the reaction mixture was diluted with roughly 15 mL of pentane, filtered two times and the solvents pentane and THF were removed by distillation under reduced pressure. Afterwards, the crude product was obtained by distillation out of the TPPO melt (oil bath temperature: 160 °C, crude product distilled at 80 °C and 160 mbar) and then fractionated with a Vigreux column (90-94 °C, 34 mbar), yielding pure IMMCH (56% yield). Figures S11-S15 show the 2D NMR analysis and the Figure S16 proves full removal of all TPPO residues by $^{31}$P NMR.




$^{1}$H (400 MHz, C*D*Cl$_3$) δ[ppm] = 5.69 (ddq, *J*=5.4, 2.8, 1.4 Hz, 1H, m), 4.90 (m, 1H, p), 4.79 (m, 1H, p), 4.74 (m, 2H, w), 2.46 (m, 1H, q), 2.30 (m, 1H, r), 2.28 (m, 1H, q), 2.20 (m, 1H, s), 2.09 (m, 1H, s), 1.82 (dt, *J*=2.4, 1.4 Hz 3H, t), 1.74 (t, *J*=1.1 Hz 3H, v).

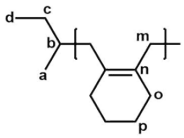
$^{13}$C (101 MHz, C*D*Cl$_3$) δ[ppm] = 149.35 (1C, U), 144.98 (1C, N), 132.63 (1C, O), 127.77 (1C, M), 109.12 (1C, W), 108.41 (1C, P), 42.25 (1C, R), 37.49 (1C, Q), 31.89 (1C, S), 20.85 (1C, V), 19.40 (1C, T).

**General Procedure for Carbanionic Polymerization**

The monomers were dried over calcium hydride and trioctylaluminium, and then distilled into a anionic flask. Polymerizations at room temperature were performed in an argon-flooded glove box and hence the solvents and reagents added volumetrically under argon atmosphere. For polymerizations at higher temperatures, the monomers were added to dried solvents in argon counterflow using syringes and the solution was tempered to the desired temperature. Afterwards, the required amount of *sec*-BuLi was added under vigorous stirring. The living chain ends were terminated by addition of methanol. The polymers were precipitated pouring the reaction solution into a 5-10-fold excess of methanol, dried at reduced pressure for at least one week and stored under the absence of light at -20 °C under argon atmosphere.

**Homopolymerization of 1,2-Dimethylenecyclohexane (PDMCH)**

Tetralin (4.6 mL) was cryotransferred into the reaction flask and the monomer DMCH (0.45 g, 0.54 mL, 4.6 mmol, 45.7 eq.) was added via a syringe under argon atmosphere. The reaction solution was heated up to 140 °C while stirring. Upon reaching the reaction temperature, the ititiator *sec*-BuLi (0.07 mL, 1.3 M, 0.09 mmol, 1 eq.) was added using a syringe and the reaction solution was stirred vigorously. After 3 hours, the polymerization was terminated adding 0.1 mL of methanol. The hot reaction solution (105 °C to preserve solubility) was precipitated into 30 mL methanol. The polymer was dried at reduced pressure a white solid was obtained in quantitative yield. The raw NMR solution did not show any sign for unreacted monomer traces. An exclusive 1,4 incorporation can be proven by 2D NMR analysis (Fig. S18-S23).




$^{1}$H (500 MHz, $C_2D_2Cl_4$) δ[ppm] = 2.11 (4H, m), 2.04 (4H, o), 1.63 (4H, p), 0.95 (3H per chain, d), 0.90 (3H per chain, a).

$^{13}$C (126 MHz, $C_2D_2Cl_4$) δ[ppm] = 130.42 (2C, N), 32.36 (2C, M), 29.72 (2C, O), 23.52 (2C, P), 18.81 (1C per chain, A), 11.39 (1C per chain, D).

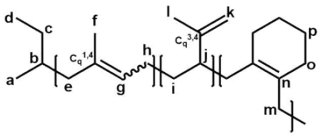
**Copolymerization of 1,2-Dimethylenecyclohexane with Isoprene (P(I-*co*-DMCH))**

The preparations of the 5 000 g·mol$^{-1}$ polymers with differing DMCH ratio were performed at room temperature inside a glove box; the preparations of the 20 000 g·mol$^{-1}$ or 40 000 g·mol$^{-1}$ polymers with 30 mol% DMCH at 40 °C or 60 °C were performed in a fume hood using Schlenk-technique. The reactions with a higher target molar mass of 20 000 and 40 000 g·mol$^{-1}$ were first conducted with an initial monomer concentration of 1.8 mol·L$^{-1}$, as done for the 5 000 g·mol$^{-1}$ polymers. Due to gelation issues, the initial monomer concentrations ($c$=($n_I$+$n_{DMCH}$)·$V_{cyclohexane}^{-1}$) had to be reduced to guarantee proper mixing and prevent gelation (see Table 2).

The procedure is exemplified for a 40 000 g·mol$^{-1}$ polymer with 40 mol% DMCH. Dried cyclohexane (62 mL for an initial monomer concentration of 1.0 M) was fleshly distilled and transferred into the reaction flask and the monomers DMCH (*exo-cis*: 2.67 g, 3.18 mL, 24.7 mmol, 190 eq.; the absolute amount of the isomeric mixture was factored in the purity determined by $^{1}$H NMR prior to use) and isoprene (2.52 g, 3.71 mL, 37.0 mmol, 285 eq.) were added via a syringe under argon atmosphere. The reaction solution

was heated up to the targeted reaction temperature abd then the ititiator *sec*-BuLi (0.10 mL, 1.3 M, 0.13 mmol, 1 eq.) was added using a syringe while stirring the reaction solution vigorously. The next day (~16 hours), the polymerization was terminated adding 0.2 mL of methanol. The polymer was precipitated into 600 mL methanol, and dried at reduced pressure. A white solid was obtained in quantitative yield. The raw NMR solution did showed complete conversion over night at elevated reaction temperatures, but unreacted DMCH traces for reactions over night at room temperature (Fig. S26). The polymers were characterized by 2D NMR, what is exemplified for one specimen (Fig. S27-S31).



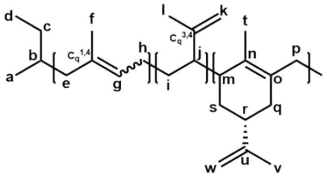
$^{1}$H (600 MHz, C*D*Cl$_3$) δ[ppm] = 5.1 (1H, g), 4.8 (1H, k), 4.7 (1H, k), 2.0 (2H, h), 2.0 (2H, $e^{cis}$), 2.0 (4H, m), 2.0 (2H, $e^{trans}$), 2.0 (4H, o), 1.7 (3H, $f^{cis}$), 1.6 (3H, $f^{trans}$), 1.6 (3H, l), 1.5 (4H, p), 1.5 (2H, i), 0.9 (3H per chain, d), 0.8 (3H per chain, a).

$^{13}$C (151 MHz, C*D*Cl$_3$) δ[ppm] = 147.6 (1C, $C_q^{3,4}$), 135.2 (1C, $C_q^{3,4}$), 130.4 (2C, N), 125.2 (1C, G), 111.6 (1C, K), 48.1 (1C, J), 39.9 (1C, $E^{trans}$), 32.6 (2C, M), 32.3 (1C, $E^{cis}$), 29.8 (2C, O), 29.1 (1C, I), 26.5 (1C, H), 23.8 (2C, P), 23.5 (1C, $F^{cis}$), 18.7 (1C per chain, A), 18.2 (1C, L), 15.7 (1C, $F^{trans}$), 11.8 (1C per chain, D).

Depending of the initial monomer concentration, the DMCH ratio and the reaction temperature, the reaction solutions became turbid or even gelated, what was tried to be avoided to ensure unhindered diffusion. However, the 0.5 M reaction solution of the 40 000 g·mol$^{-1}$ polymer 40 mol% was turbid, but of comparatively low viscosity and hence still stirrable.

**Copolymerization of (*5R*)-5-isopropenyl-2-methyl-1-methylene-2-cyclohexene with Isoprene (P(I-*co*-IMMCH))**

All reactions were performed inside a glove box. Cyclohexane (6.6 mL), the monomers IMMCH (1.00 mL, 0.88 g, 5.94 mmol, 22.8 eq.) and isoprene (0.59 mL, 0.40 g, 5.94 mmol, 22.8 eq.) and in three out of four cases the modifier THF (0.04 mL, 2 eq. / 0.42 mL, 20 eq. / 4.22 mL, 200 eq.) were transferred into a glass vial equipped with a magnetic stirrer and sealed with a septum cap. Next, the ititiator *sec*-BuLi (0.20 mL, 1.3 M, 0.26 mmol, 1 eq.) was added under stirred vigorously. After 24 hours, the polymerization was terminated adding 0.3 mL of methanol. The polymer was precipitated into 50 mL methanol. The polymer was dried at reduced pressure giving a colorless viscous liquid. The NMR of the raw raction solutions (Fig. S32 exemplified for the reaction without THF) and also of the precipitated polymers revealed that no isoprene was left after polymerization, but IMMCH remained within the reaction solution unreacted (integral ratio of PI(g)/IMMCH(*m*) (1.00/0.92)). Homopolymerization experiments of IMMCH in cyclohexane, mixtures of cyclohexane with 2, 20 or 200 equivalents of THF and pure THF at room temperature failed. The polymers were characterized by 2D NMR, what is exemplified for one specimen (Fig. S35S-S39).



$^{1}$H (600 MHz, C*D*Cl$_3$) δ[ppm] = 5.3 (1H, g), 4.9 (2H, k), 2.2 (2H, h), 2.2 (2H, $e^{cis}$), 2.1 (2H, $e^{trans}$), 2.1 (1H, j), 1.8 (3H, $f^{cis}$), 1.7 (3H, $f^{trans}$), 1.7 (3H, l), 1.5 (2H, i), 0.9 (3H per chain, d), 0.9 (3H per chain, a).

$^{13}$C (151 MHz, C*D*Cl$_3$) δ[ppm] = 147.6 (1C, $C_q^{3,4}$), 135.2 (1C, $C_q^{3,4}$), 125.4 (1C, G), 111.7 (1C, K), 48.1 (1C, J), 40.1 (1C, $E^{trans}$), 32.4 (1C, $E^{cis}$), 31.4 (1C, I), 26.7 (1C, H), 23.5 (1C, $F^{cis}$), 19.2 (1C per chain, A), 18.5 (1C, L), 16.0 (1C, $F^{trans}$), 11.5 (1C per chain, D).

**Supporting Information obtained by DFT Calculations**

Figure S1 summarizes the Loewdin electron densities, the dihedral angle between the two double bonds as well as the 3D visualization of the monomers used. In the case of DMCH, both the chair as well as the boat conformation are shown.
Figure S2 illustrates the arrangement of the living PDMCH-Li chain end with a DMCH monomer molecule during the reaction pathway, showing the 3D geometries during polymerization and assigning these structures to different stages of the reaction progress. Here, the residual chain is simplified as a methyl group and only the terminal unit, i.e., DMCH, is specified.

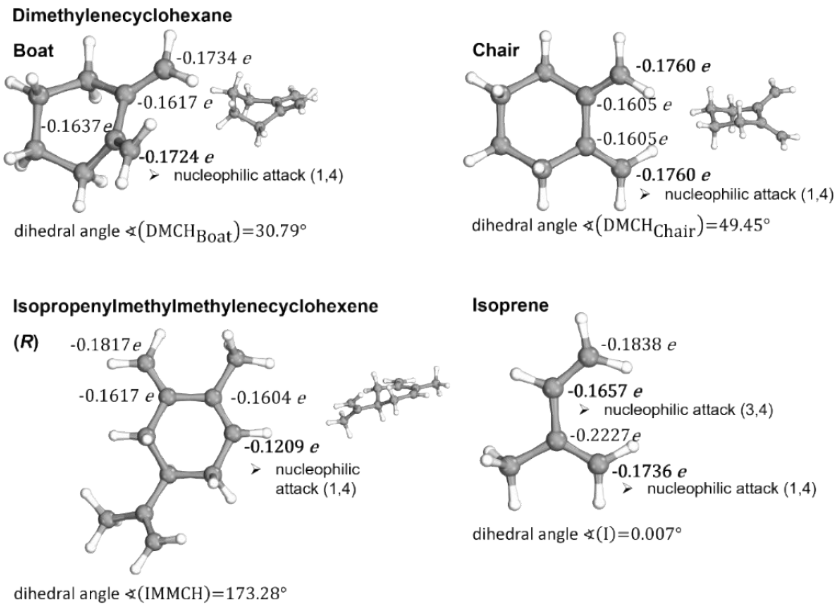



**Figure S1.** Chemical structures of the monomers dimethylenecyclohexane (DMCH), (5*R*)-5-isopropenyl-2-methyl-1-methylene-2-cyclohexene (IMMCH) and isoprene (I) with assigned partial charges and dihedral angle between the double bonds obtained by DFT calculations.

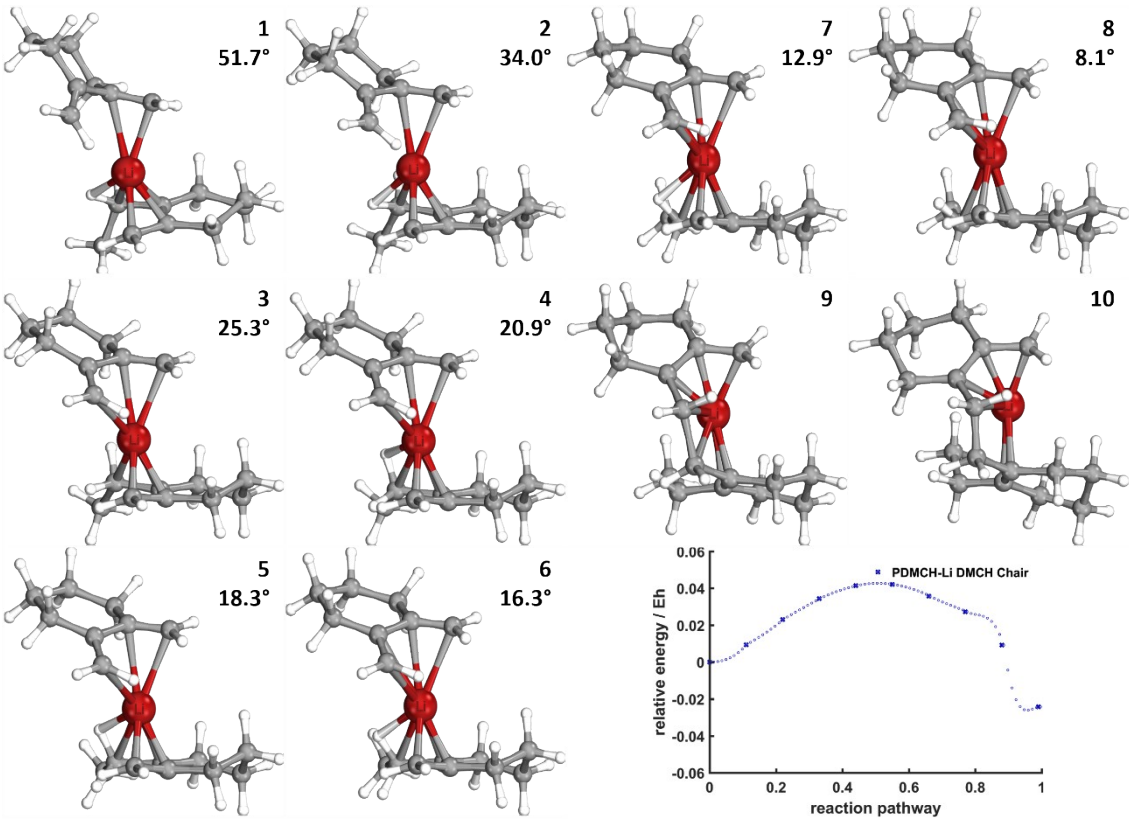



**Figure S2.** 3D visualization of the chemical structures along the reaction pathway of the DMCH homopropagation (PDMCH-Li + DMCH) obtained by DFT calculations. The dihedral angle between the double bonds is noted below the corresponding stage of reaction progress (values of x-axis: 0.00, 0.11, 0.22, 0.33, 0.44, 0.55, 0.66, 0.77, 0.88, 0.99 that are marked with a cross). For simplification and less computing effort, the residual chain is simulated by a methyl group, which is why influences of repeating units except the ultimate one are neglected.

**Supporting Information concerning the in situ $^1$H NMR kinetics**

Figure S3 contains the plots of the logarithmic reciprocal concentration and the relative concentraions over time, respectively. Figure S4 shows all plots for kinetical investigations at 40 and 60 °C, that were performed at higher initiator concentrations of (one drop of a 1.3M *sec*-BuLi solution), demonstrating the comparably speeded up reaction compared to room temperature.

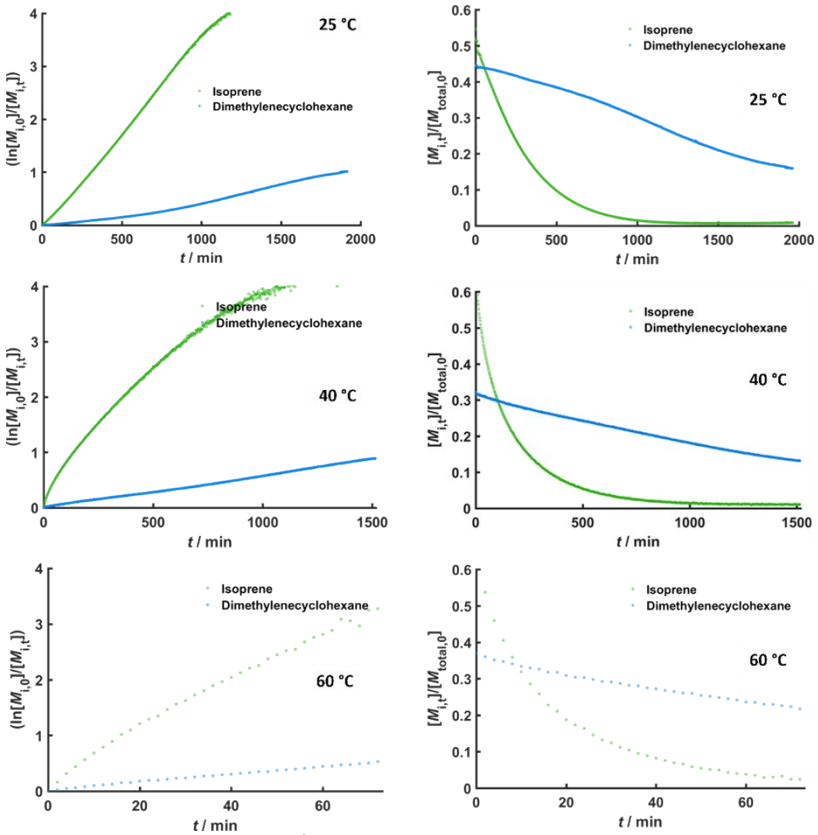



**Figure S3.** Left: Plot of the logarithmic reciprocal concentration $\ln([M_0]/[M_t])$ over time for both monomers isoprene (green) and DMCH (blue). Right: Plot of the relative concentrations ($[M_t]/[M_0]$) over time for both monomers isoprene (green) and DMCH (blue). Top: Copolymerization at 25 °C, initiated with a 1.3M *sec*-BuLi solution. Middle, bottom: Copolymerizations at 40 and 60 °C, respectively, initiated with a 0.13M *sec*-BuLi solution.

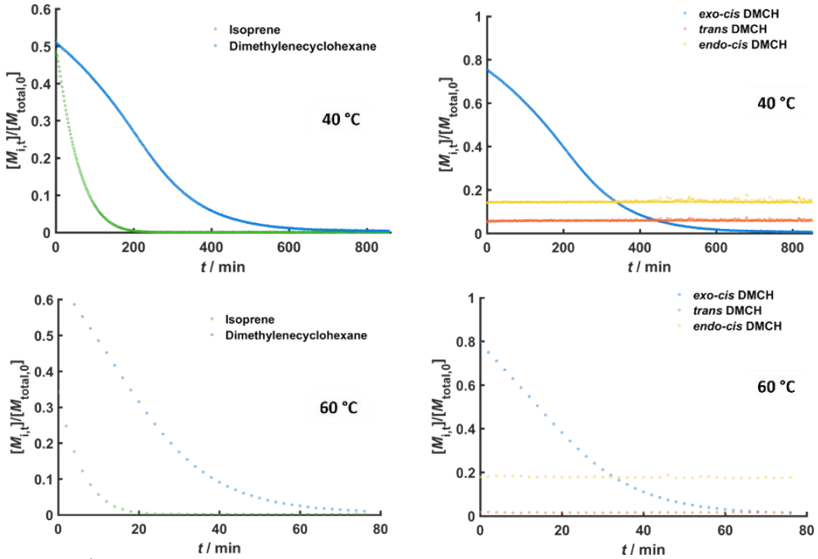



**Figure S4.** Left: Plot of the concentration $[M_{i,t}]/[M_{total,0}]$ over time for both monomers isoprene (green) and DMCH (blue). Right: Plot of the relative concentration $[M_t]/[M_0]$ over time for the three DMCH isomers *exo-cis* (blue), *endo-cis* (yellow) and *trans* (orange). Both kinetics were initiated with a 1.3M *sec*-BuLi solution.

**NMR spectra of DMCH**

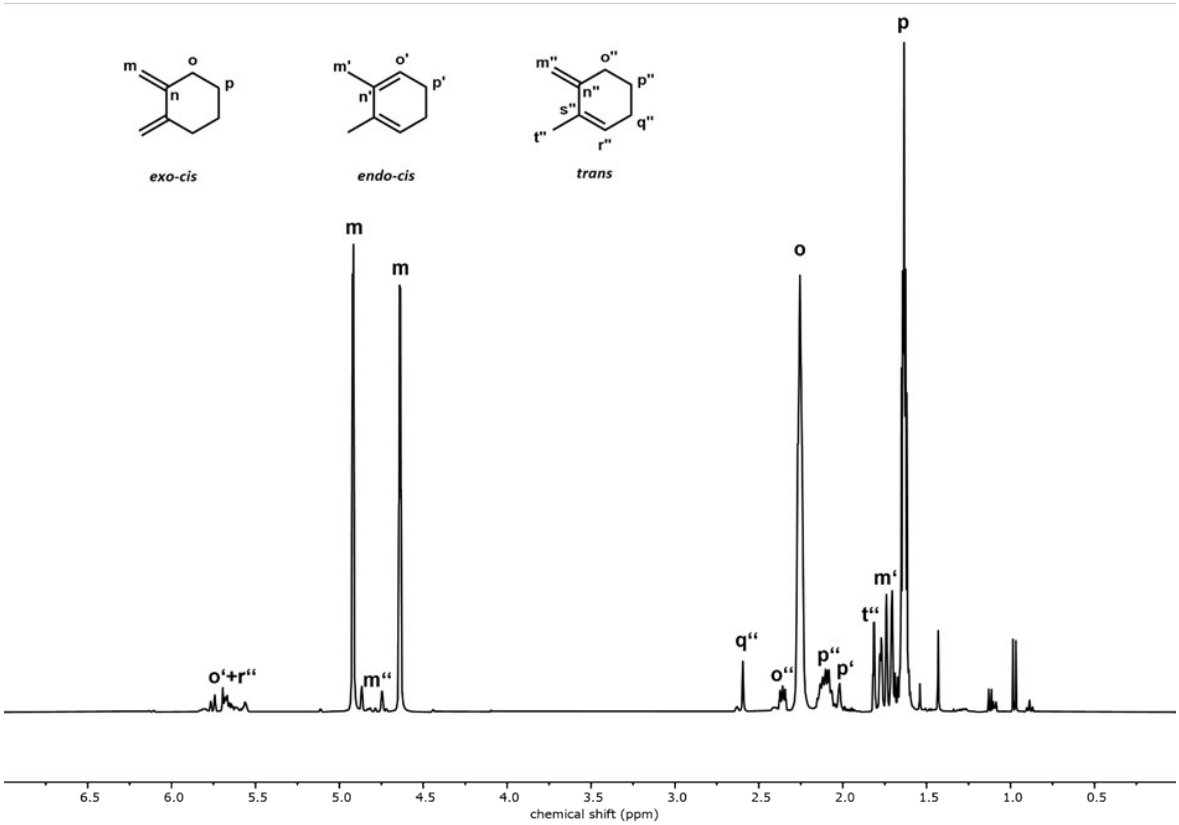



**Figure S5.** $^{1}$H-NMR spectrum (400 MHz, $CDCl_3$) of *exo-cis* DMCH and its isomers *endo-cis* DMCH and *trans* DMCH. The mixture is enriched in the reactive isomer *exo-cis* DMCH.

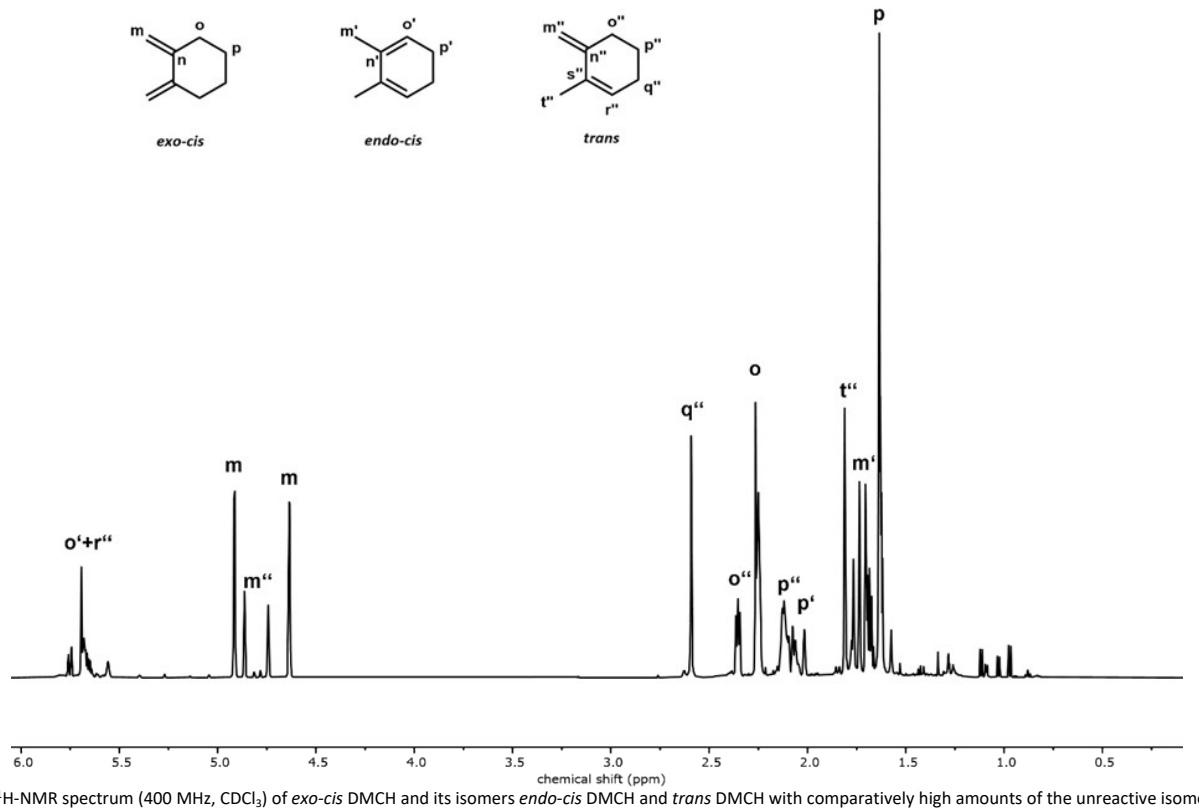



**Figure S6.** $^{1}$H-NMR spectrum (400 MHz, $CDCl_3$) of *exo-cis* DMCH and its isomers *endo-cis* DMCH and *trans* DMCH with comparatively high amounts of the unreactive isomers.

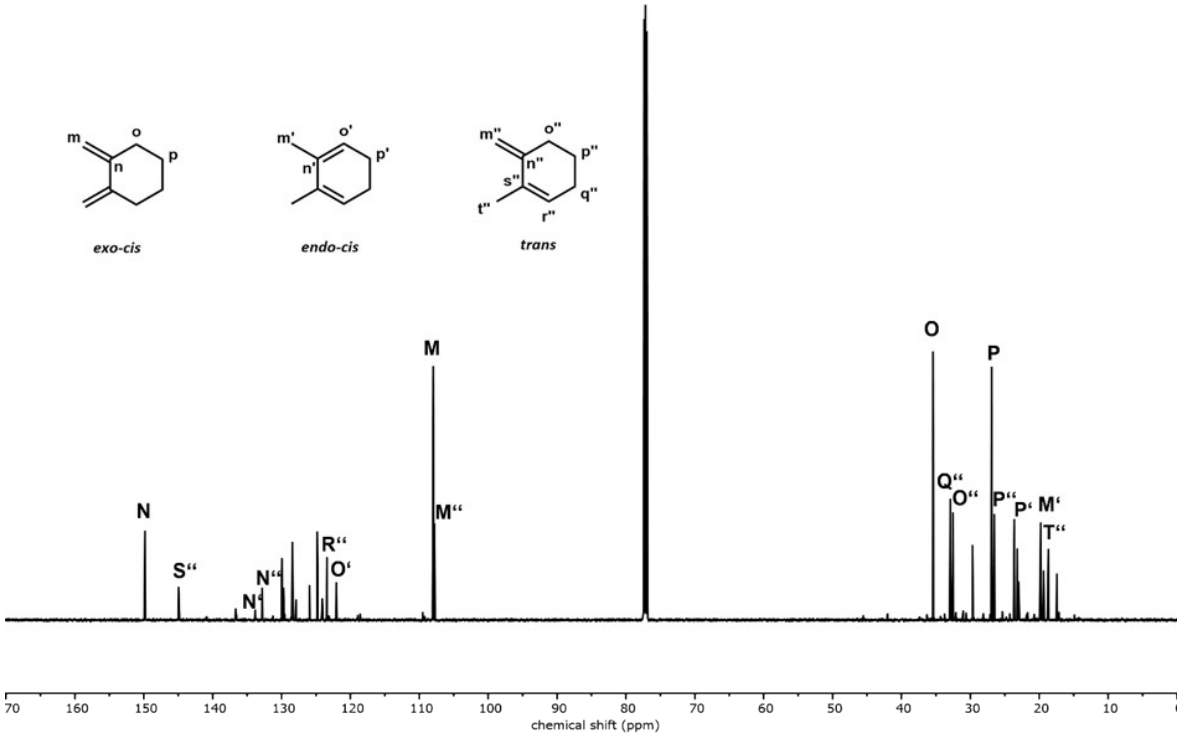



**Figure S7.** $^{13}$C-NMR spectrum (101 MHz, $CDCl_3$) of *exo-cis* DMCH and its isomers *endo-cis* DMCH and *trans* DMCH. The mixture contains comparatively high amounts of the unreactive isomers endo*-cis* and *trans* DMCH to facilitate assignments.

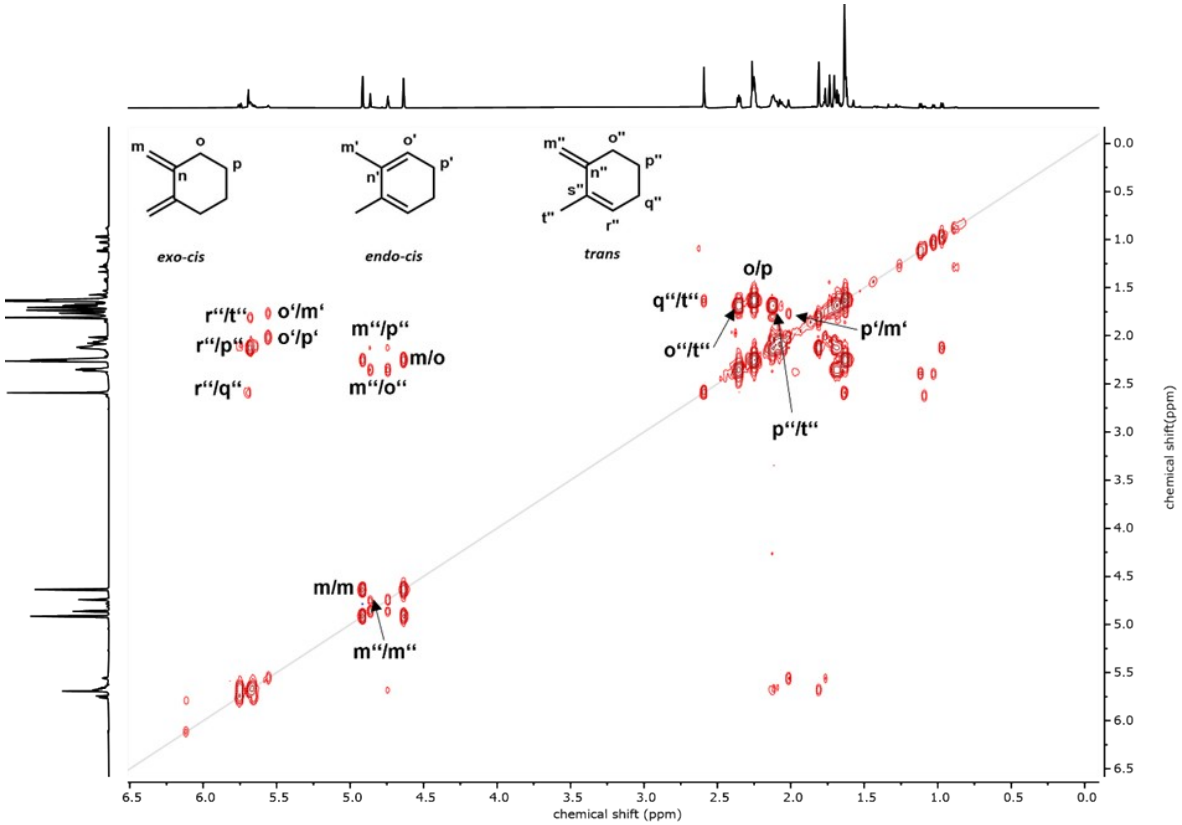



**Figure S8.** $^{1}$H$^{1}$H-COSY-NMR spectrum (400 MHz, $CDCl_3$) of *exo-cis* DMCH and its isomers *endo-cis* DMCH and *trans* DMCH. The mixture contains comparatively high amounts of the unreactive isomers endo*-cis* and *trans* DMCH to facilitate assignments.

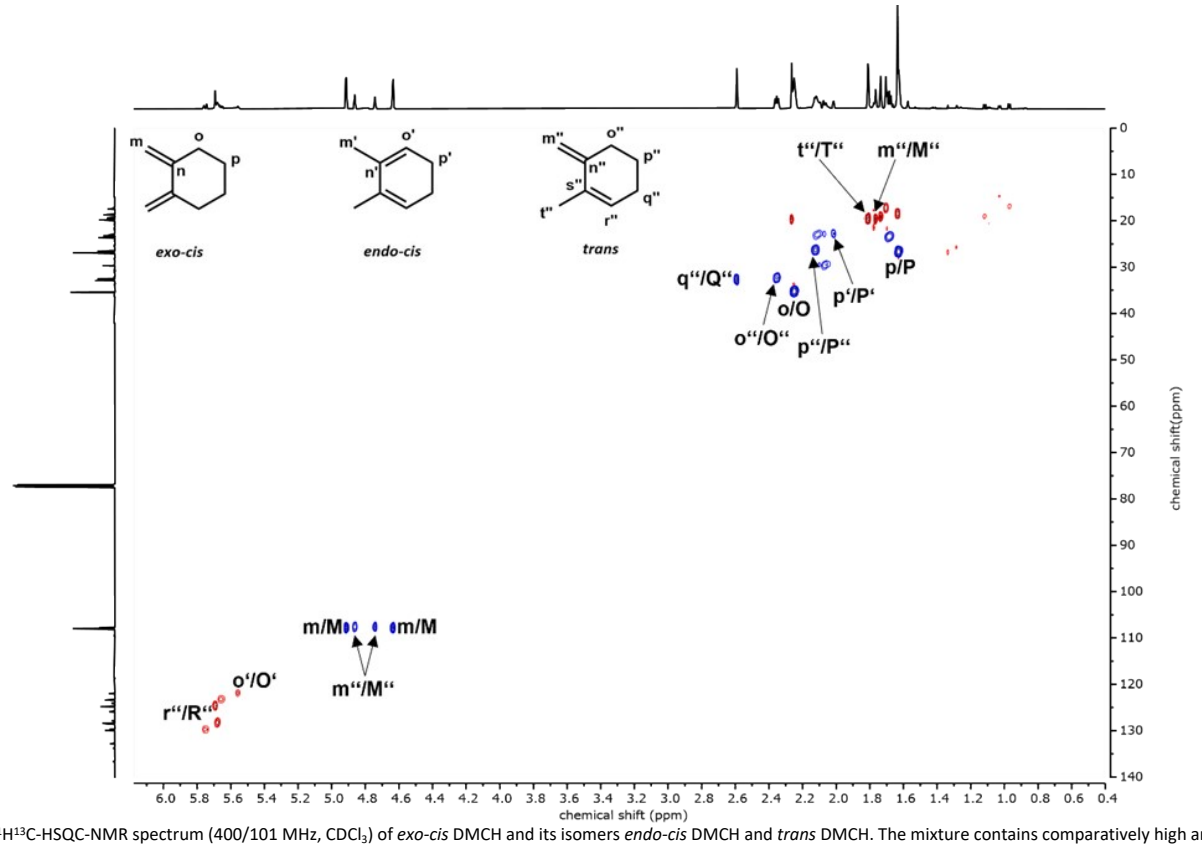



**Figure S9.** $^{1}H^{13}C$-HSQC-NMR spectrum (400/101 MHz, $CDCl_3$) of *exo-cis* DMCH and its isomers *endo-cis* DMCH and *trans* DMCH. The mixture contains comparatively high amounts of the unreactive isomers endo-*cis* and *trans* DMCH to facilitate assignments.

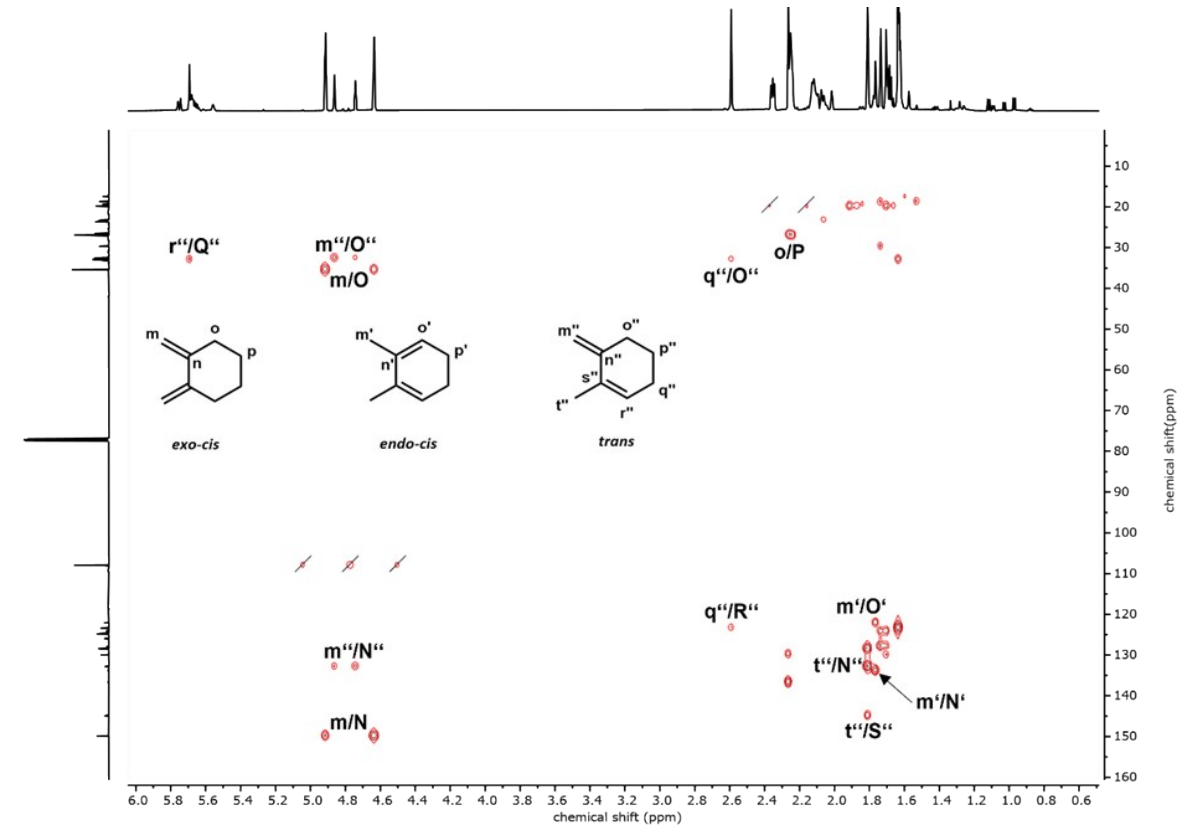



**Figure S10.** $^{1}H^{13}C$-HMBC-NMR spectrum (400/101 MHz, $CDCl_3$) of *exo-cis* DMCH and its isomers *endo-cis* DMCH and *trans* DMCH. The mixture contains comparatively high amounts of the unreactive isomers endo-*cis* and *trans* DMCH to facilitate assignments.

**NMR spectra of IMMCH**

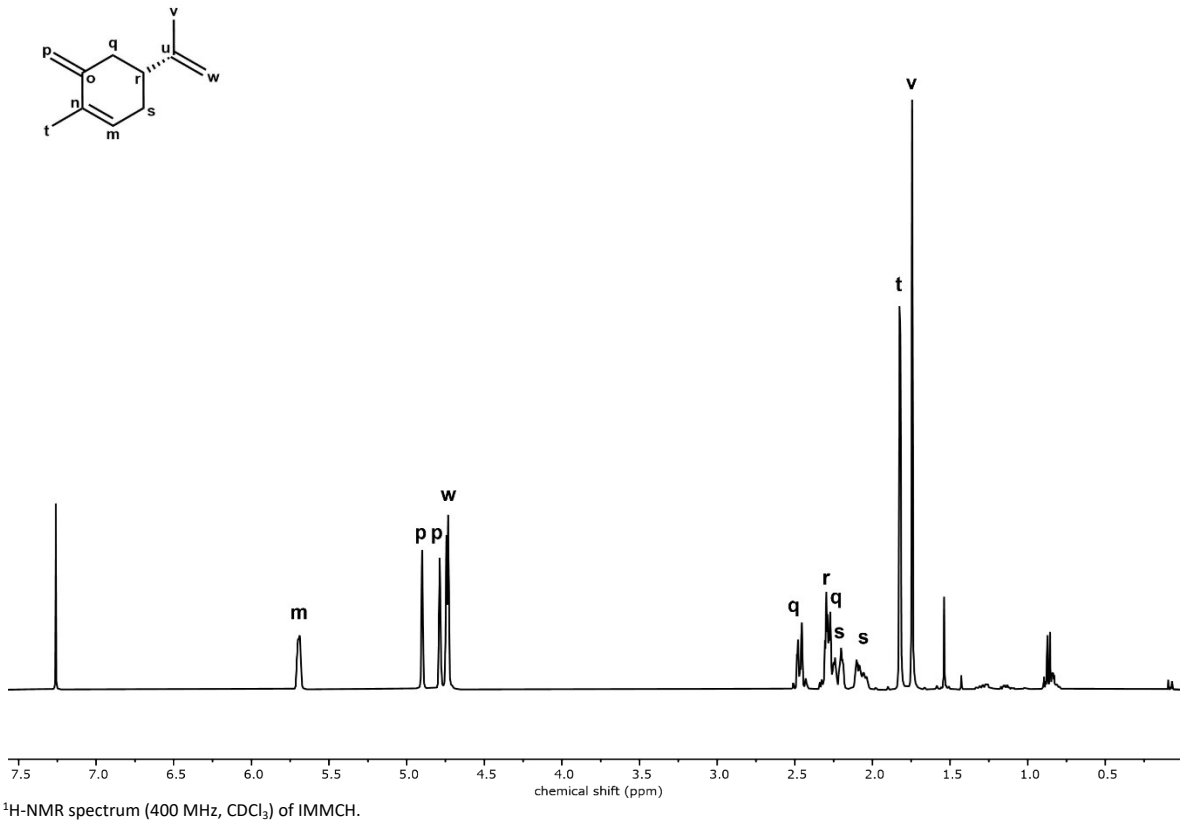



**Figure S11.** $^{1}$H-NMR spectrum (400 MHz, $CDCl_3$) of IMMCH.

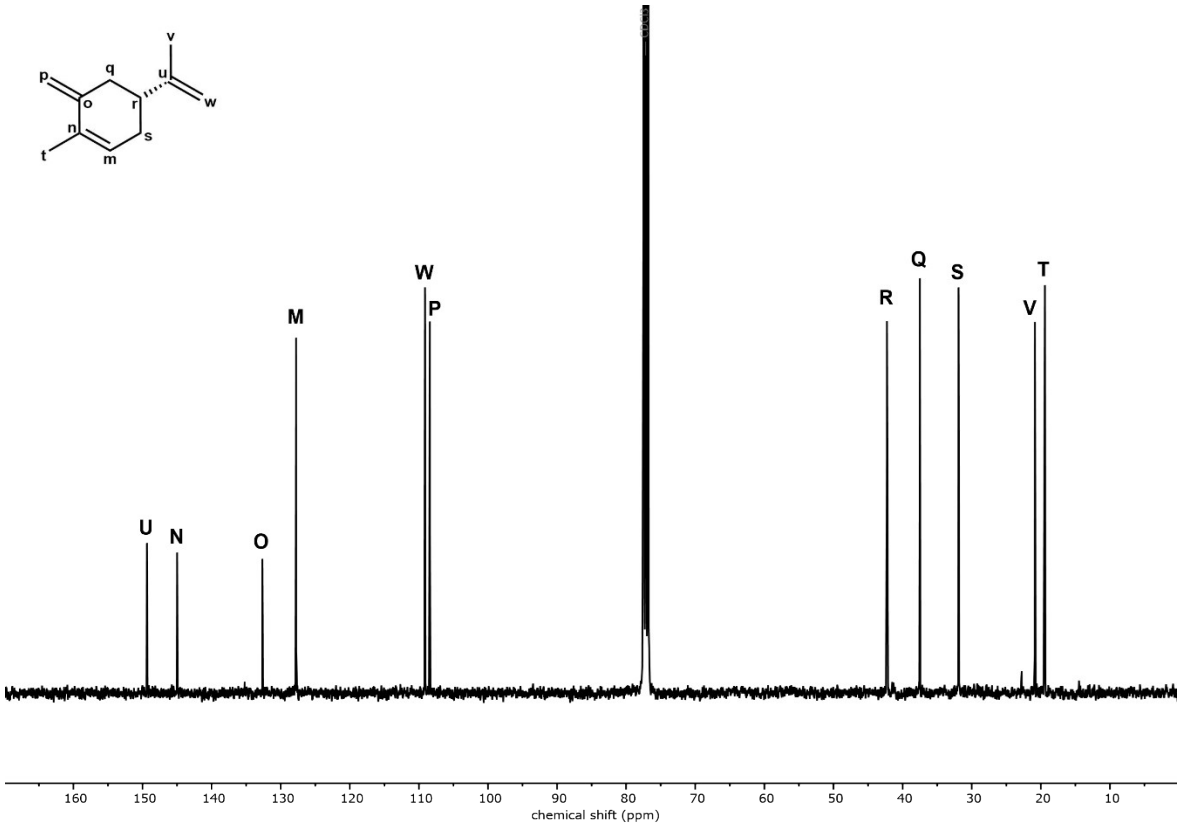



**Figure S12.** $^{13}$C-NMR spectrum (101 MHz, $CDCl_3$) of IMMCH.

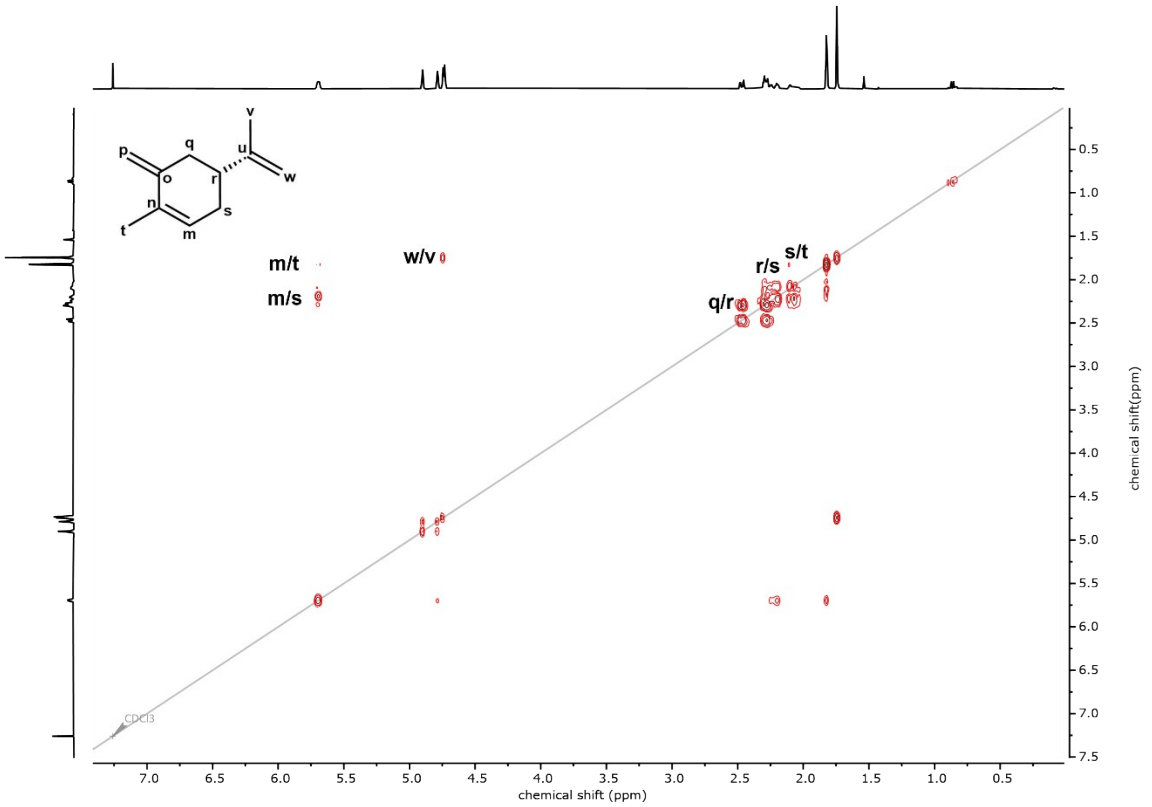



**Figure S13.** $^{1}H^{1}H$-COSY-NMR spectrum (400 MHz, $CDCl_3$) of IMMCH.

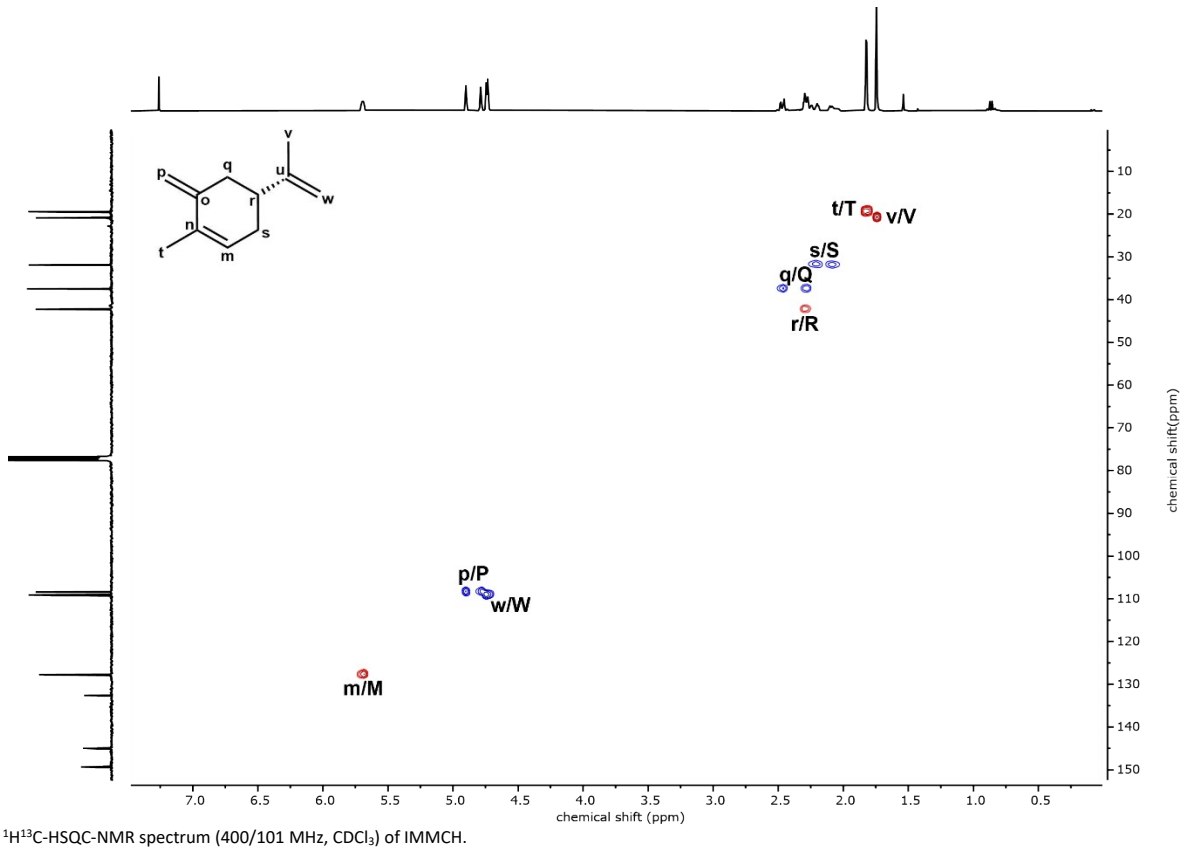



**Figure S14.** $^{1}H^{13}C$-HSQC-NMR spectrum (400/101 MHz, $CDCl_3$) of IMMCH.

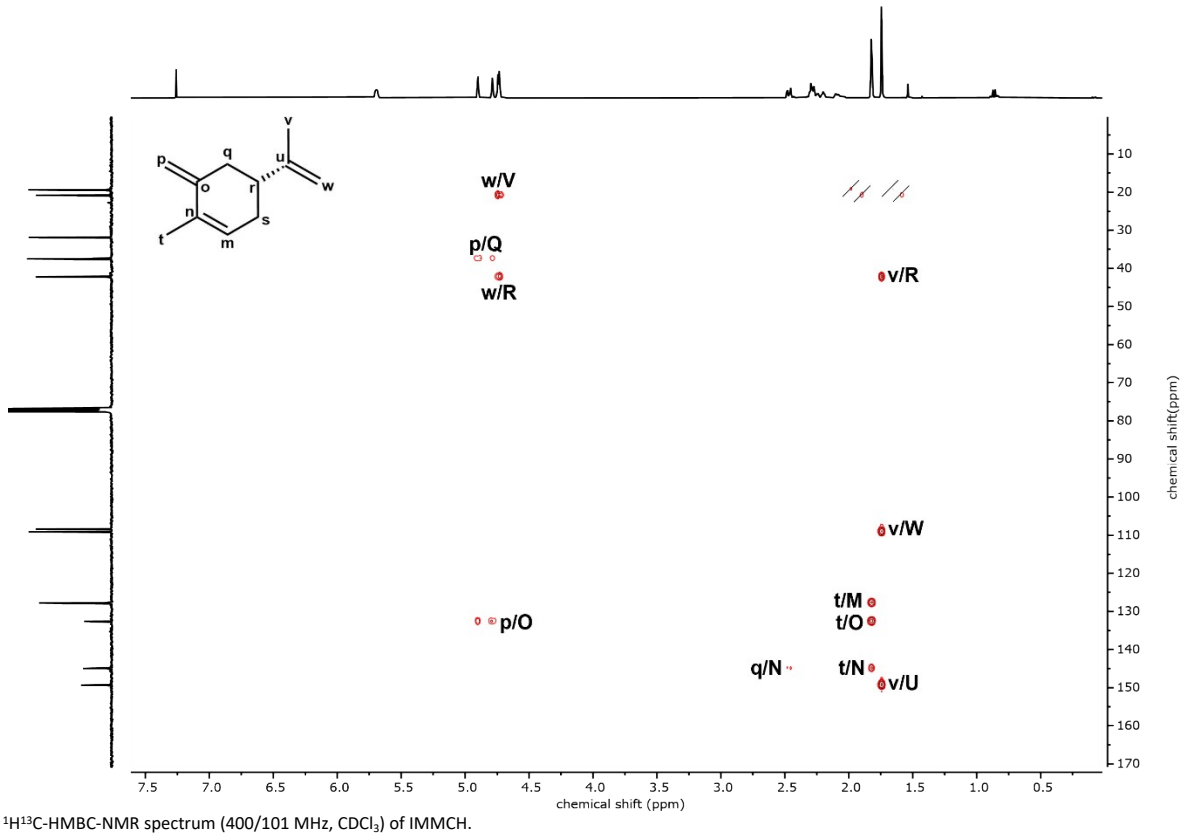



**Figure S15.** $^{1}H^{13}C$-HMBC-NMR spectrum (400/101 MHz, $CDCl_3$) of IMMCH.

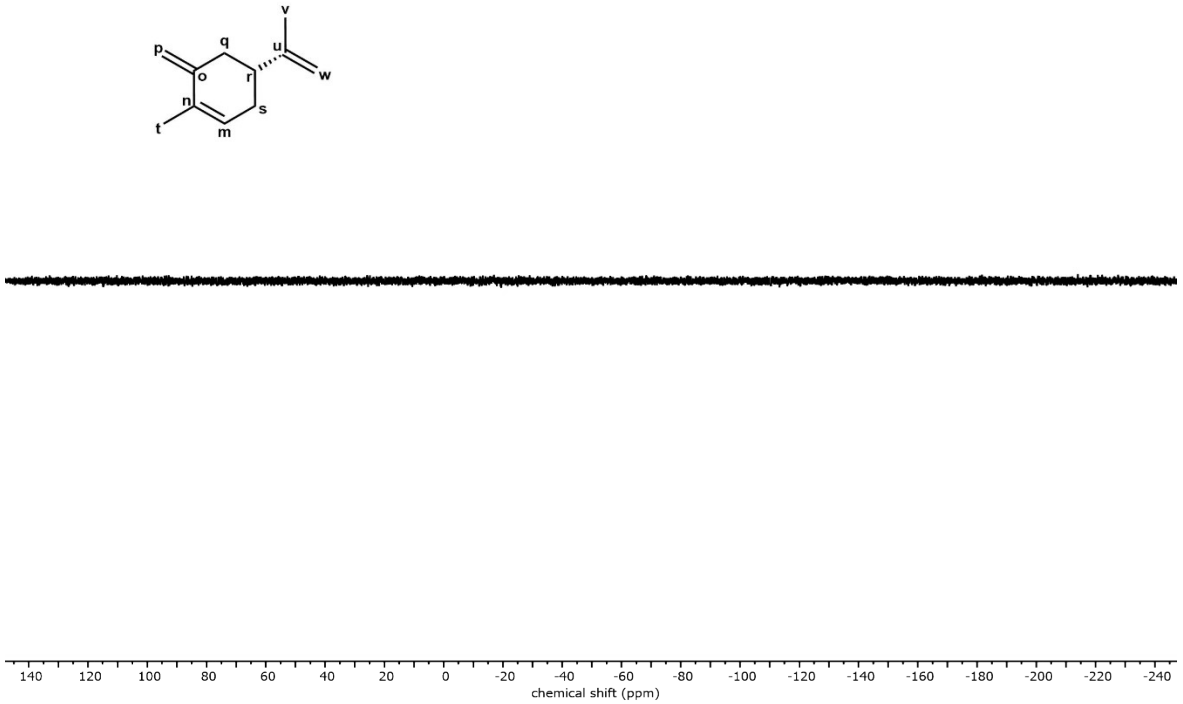



**Figure S16.** $^{31}P$-NMR spectrum (162 MHz, $CDCl_3$) of IMMCH proving that no TPPO residues are present.

**MALDI-ToF spectrum and NMR spectra of PDMCH**

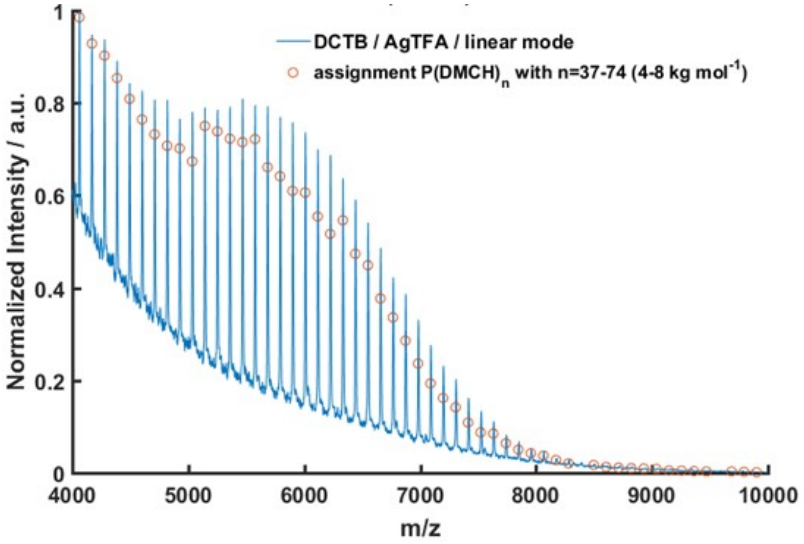



**Figure S17.** MALDI-ToF mass spectrum of PDMCH homopolymer. Matrix: DCTB, ionization agent: AgTFA, mode: linear.

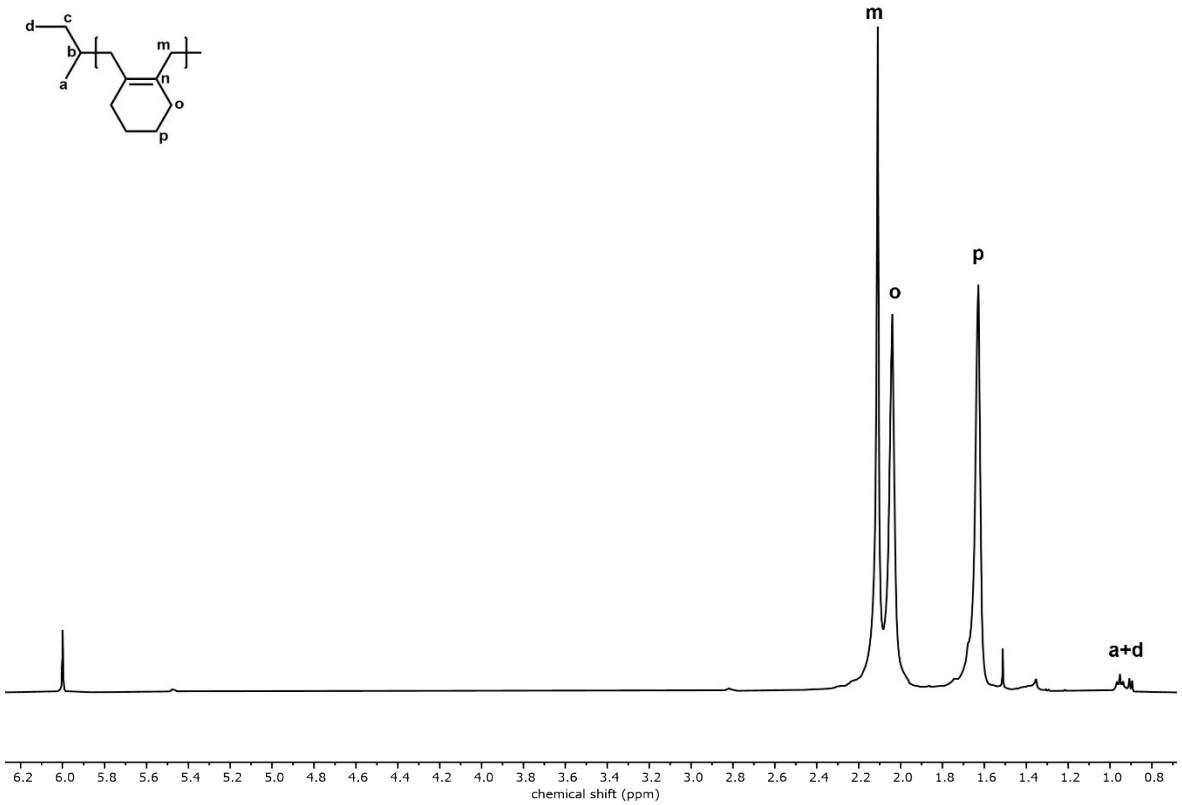



**Figure S18.** $^{1}$H-NMR spectrum (500 MHz, $C_2D_2Cl_4$) of PDMCH measured at 100 °C.

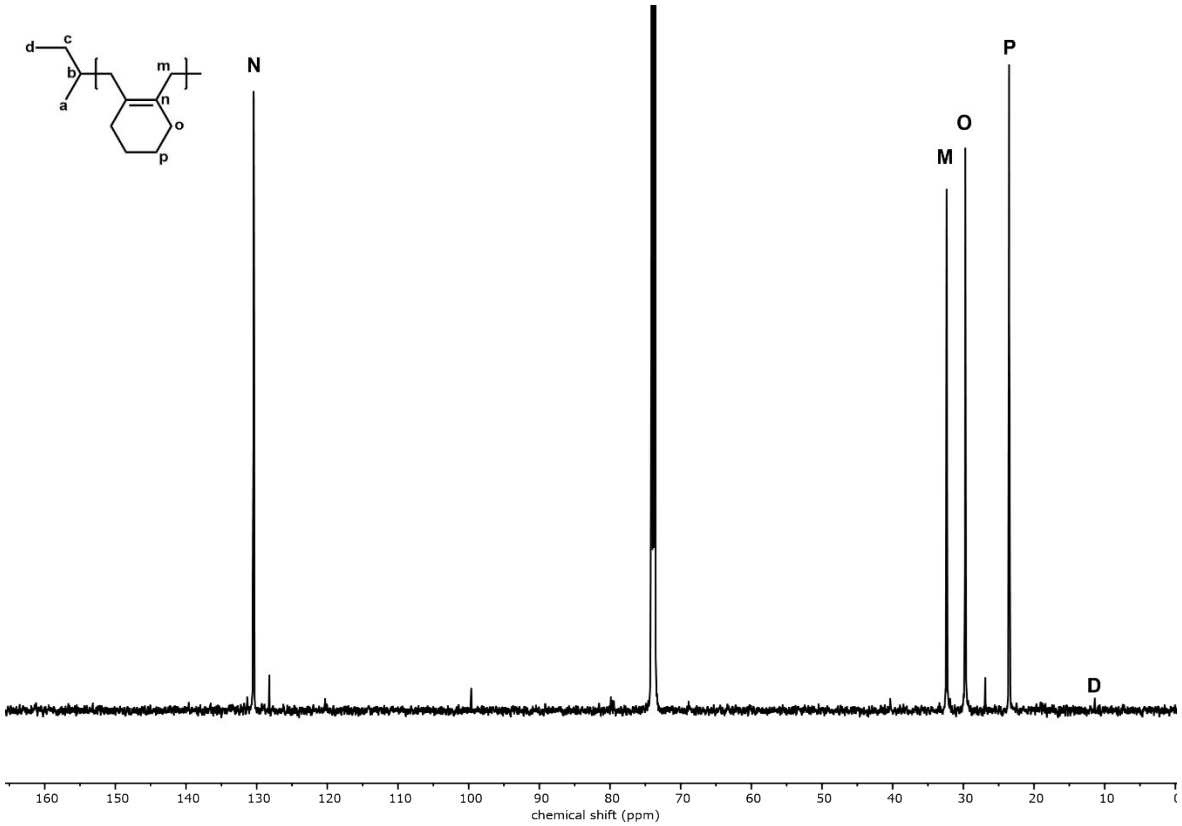



**Figure S19.** Inverse gated $^{13}$C-NMR spectrum (125 MHz, $C_2D_2Cl_4$) of PDMCH measured at 100 °C.

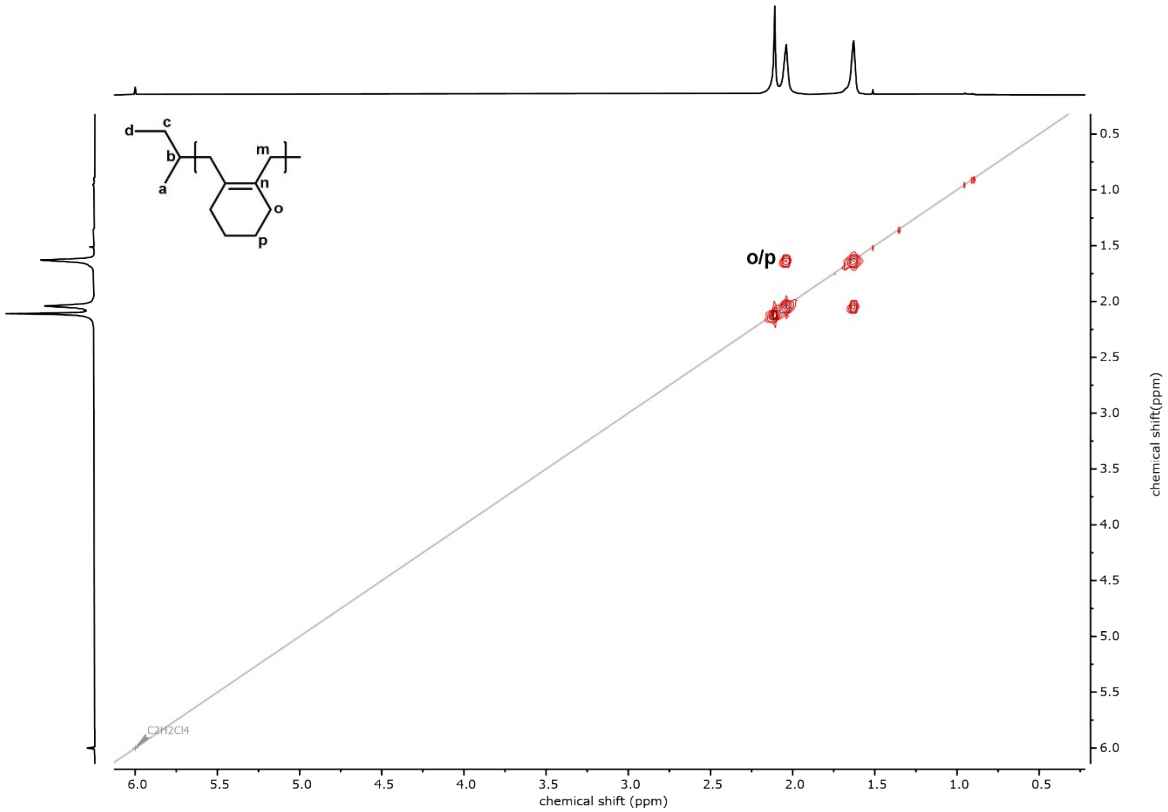



**Figure S20.** $^1$H$^1$H-COSY-NMR spectrum (500 MHz, $C_2D_2Cl_4$) of PDMCH measured at 100 °C.

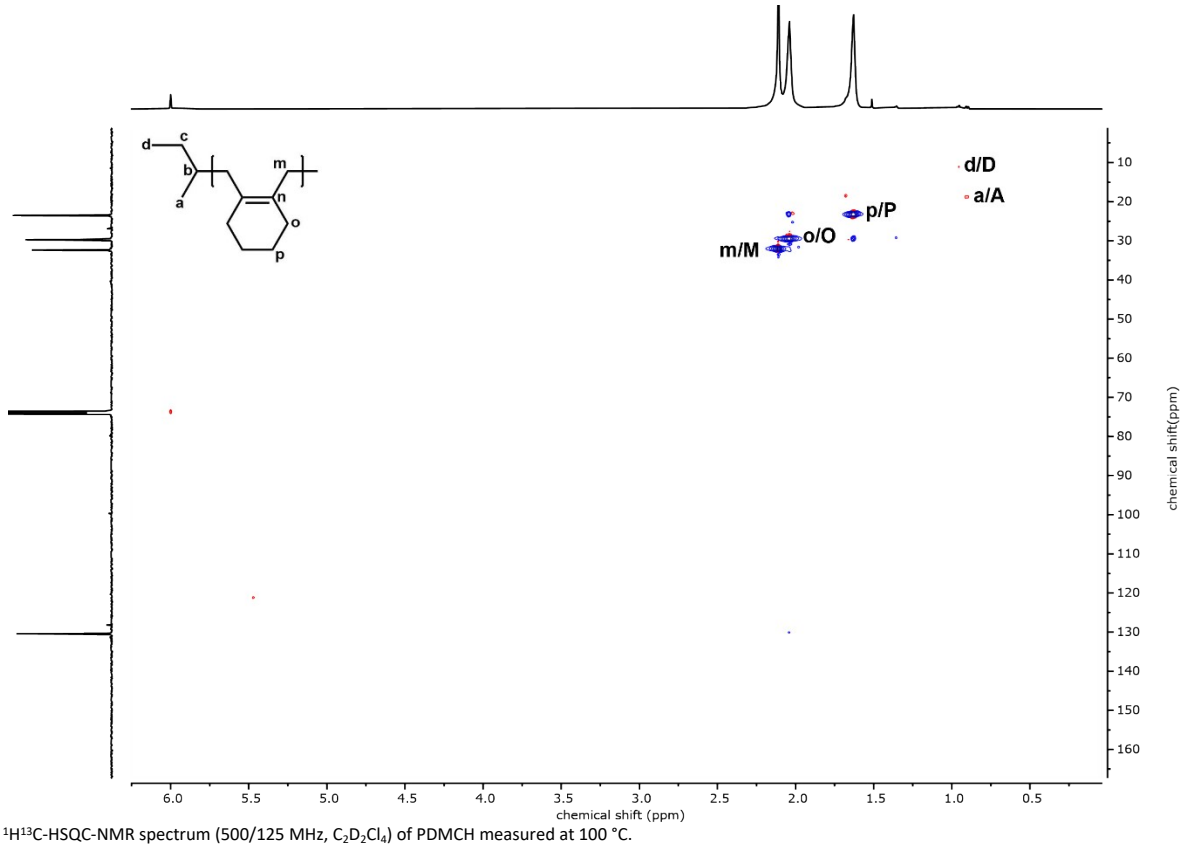



**Figure S21.** $^{1}H^{13}C$-HSQC-NMR spectrum (500/125 MHz, $C_2D_2Cl_4$) of PDMCH measured at 100 °C.

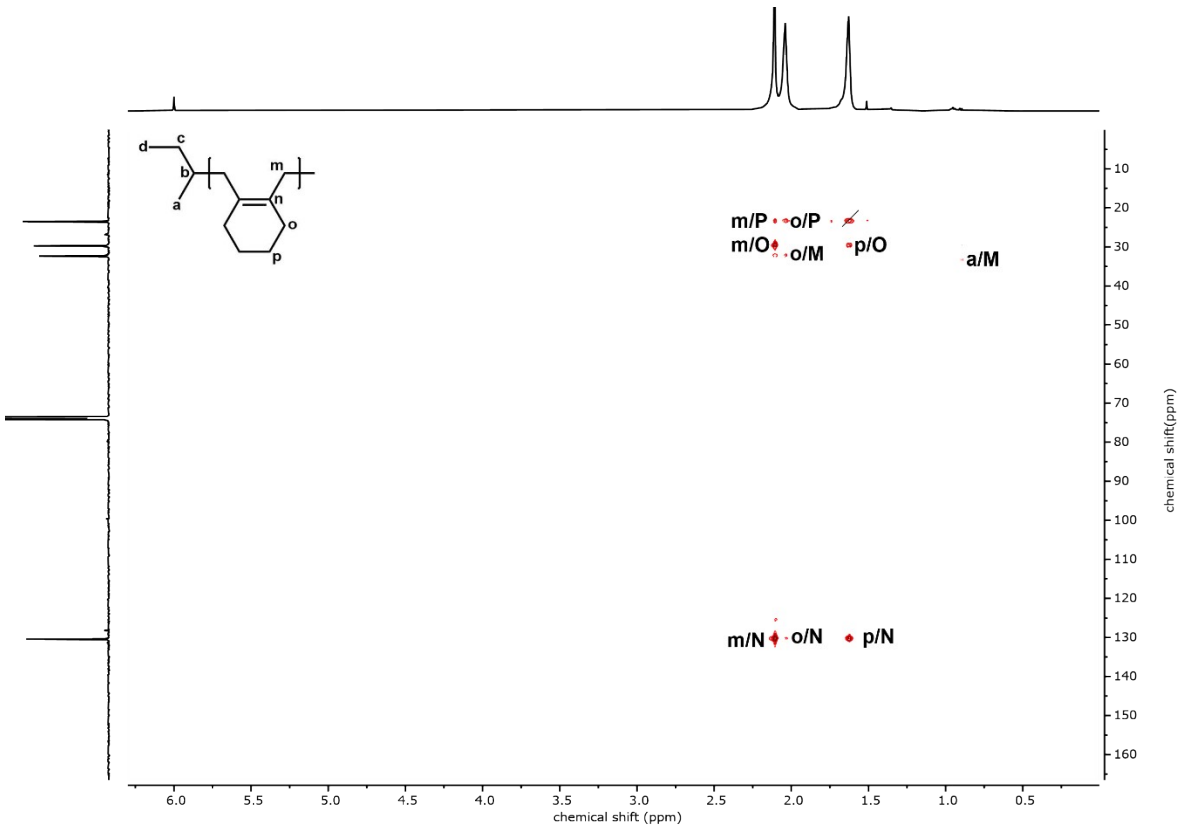



**Figure S22.** $^{1}H^{13}C$-HMBC-NMR spectrum (500/125 MHz, $C_2D_2Cl_4$) of PDMCH measured at 100 °C.

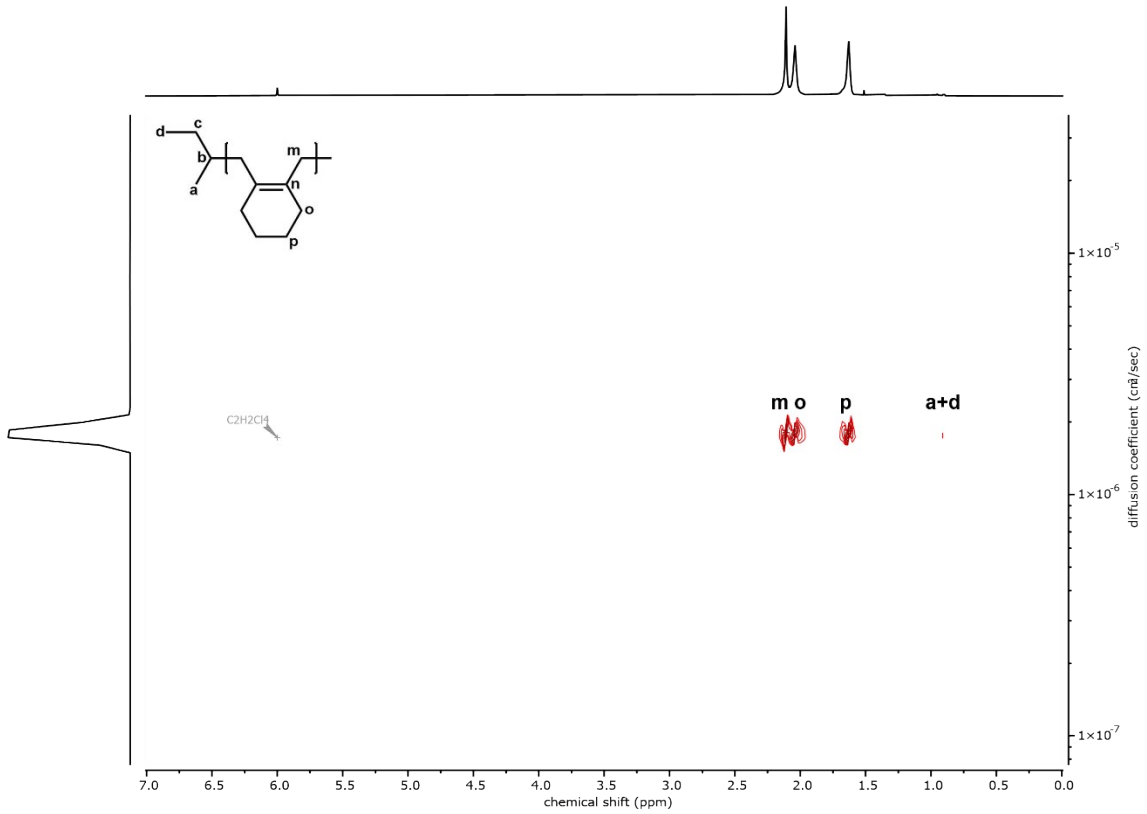



**Figure S23.** $^{1}$H-DOSY-NMR spectrum (500 MHz, $C_2D_2Cl_4$) of PDMCH measured at 100 °C.

**SEC measurements and NMR spectra of P(I-*co*-DMCH)**

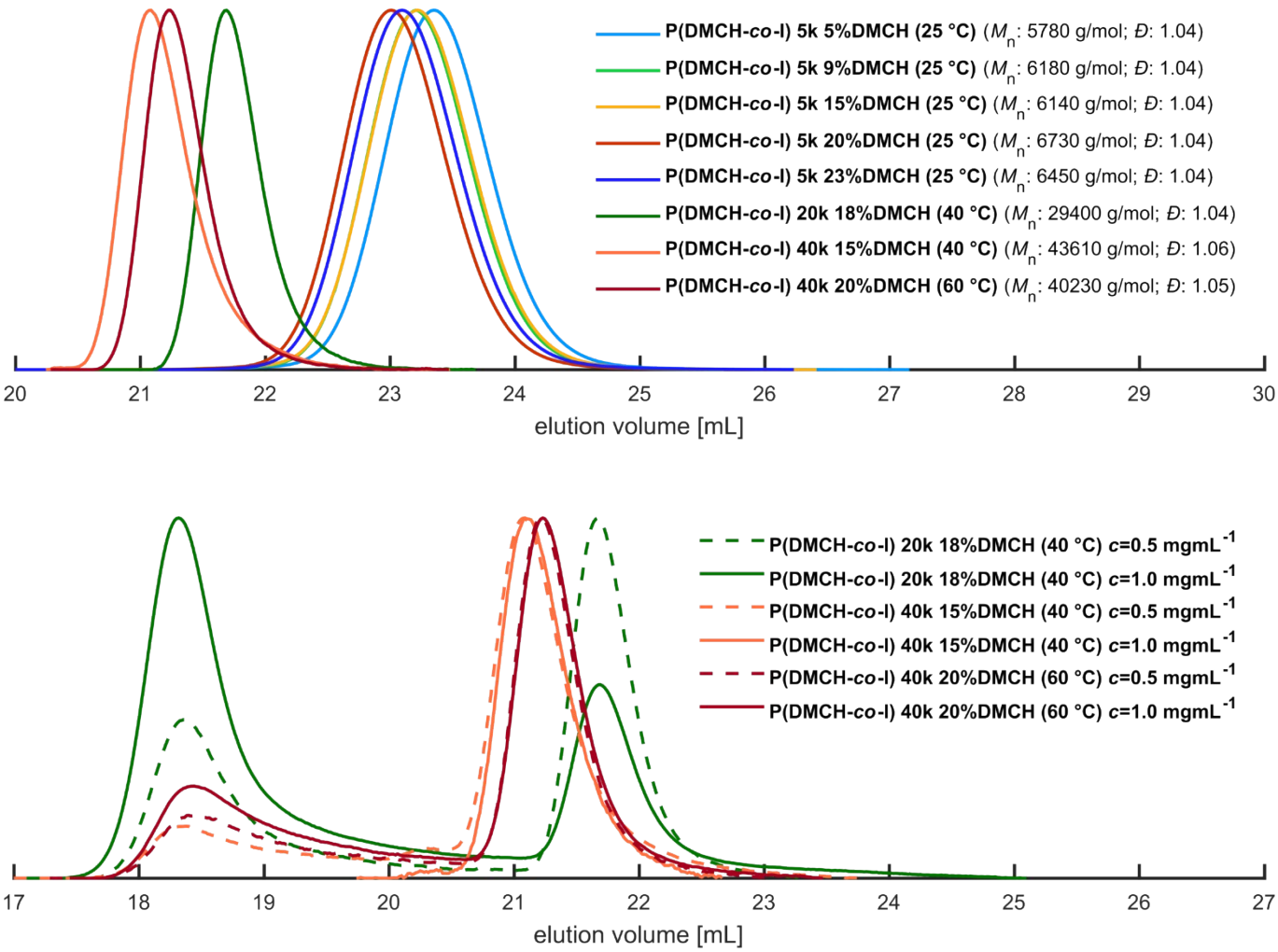



**Figure S24.** SEC traces (eluent: THF, detector: RI, calibration standard: PI) of the polymers obtained by copolymerization of isoprene and DMCH in cyclohexane. The SEC traces of copolymer of hifher molecular weights show multimodality (bottom), what could be caused by partial aggregation of the polymer in THF. To reinforce this assumption, SEC measurements were performed at concentrations of 0.5 (dashed lines) and 1.0 mg·mL$^{-1}$ (solid lines) and the relative intensity of the peaks was compared. The alteration of this ratio with the concentration supports this theory, wherefore only th main peak (top) is taken into account to determine the individual molar masses and dispersities.

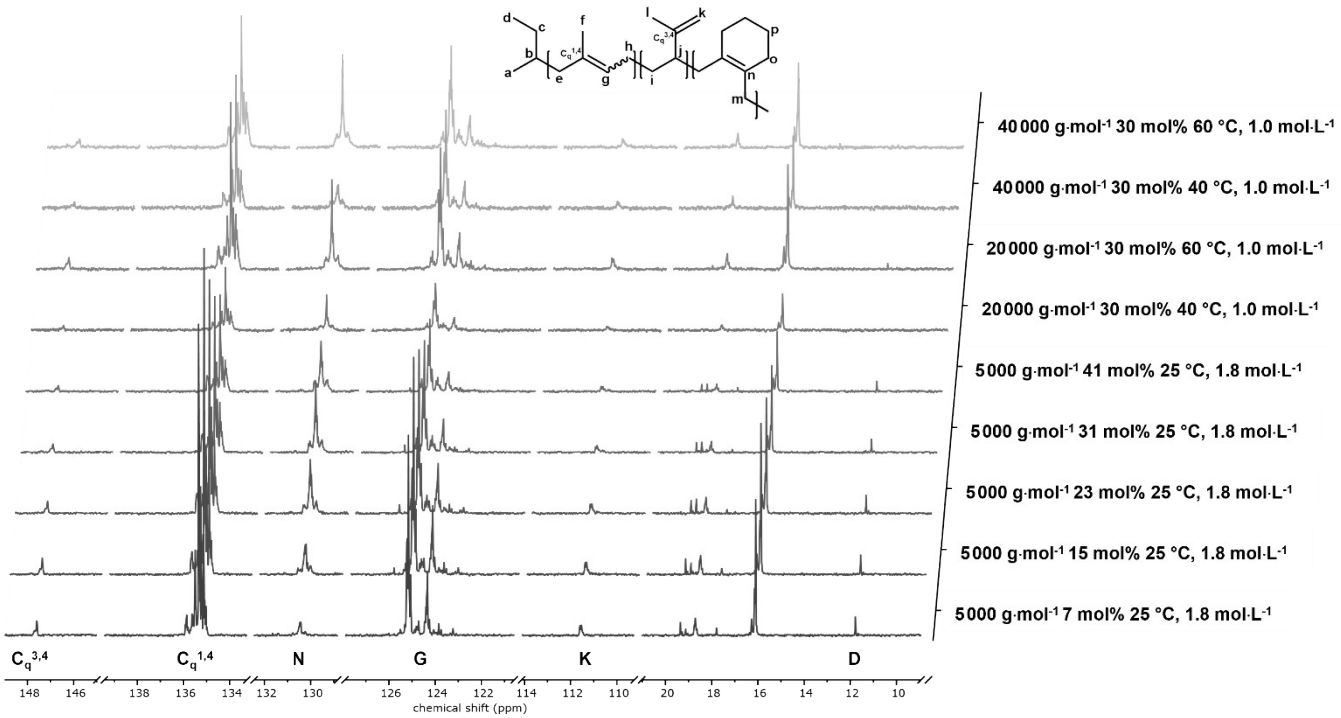



**Figure S25.** Inverse gated $^{13}$C-NMR spectra (151 MHz, d1=10 s, $CDCl_3$) of the polymers obtained by copolymerization of isoprene and DMCH in cyclohexane. The signals evaluated for the determination of the molar mass or incorporation ratio of isoprene and DMCH are shown.

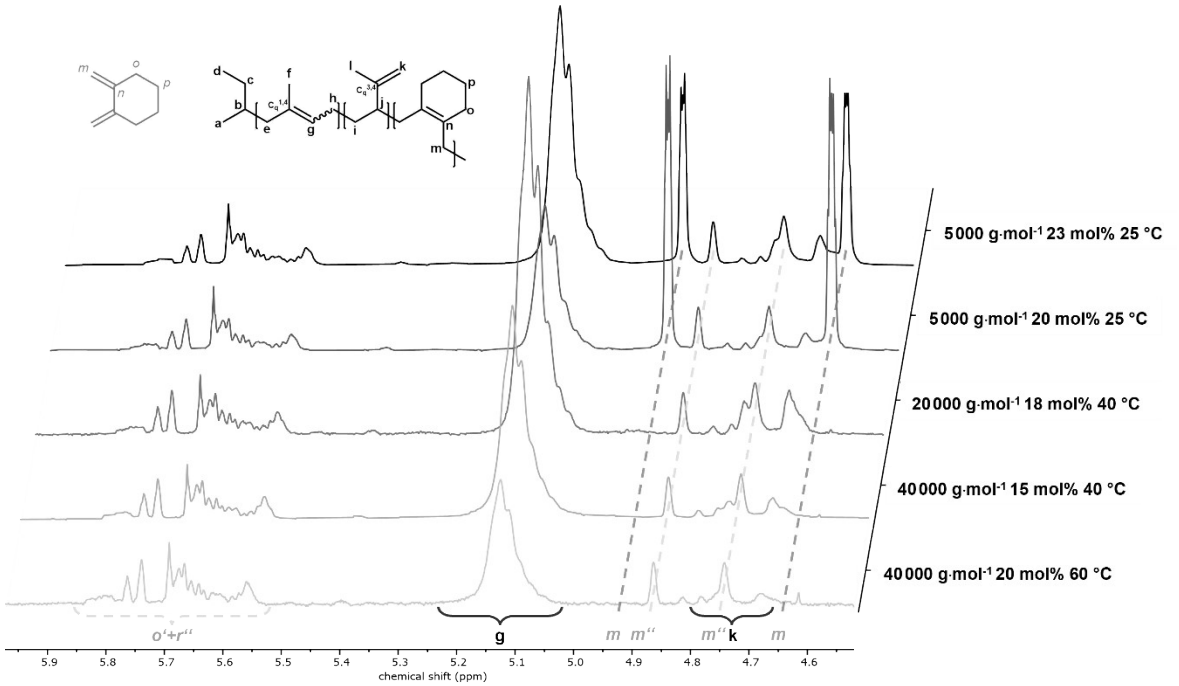



**Figure S26.** $^1$H-NMR spectrum (400 MHz, $CDCl_3$) of the raw reaction solutions of the copolymerization experiments of isoprene and DMCH. Residual monomer signals are assigned in italic and grey; polymer signals are denoted in black. Since the methylene protons of *cis-exo* DMCH are still visible in the case of the two spectra of the top, it can be concluded that the copolymerization was not completed after one night at room temperature, although the reaction solutions were higher concentrated. The raw reaction solutions of the polymerization experiments at 40 °C or 60 °C show no sign of residual monomers.

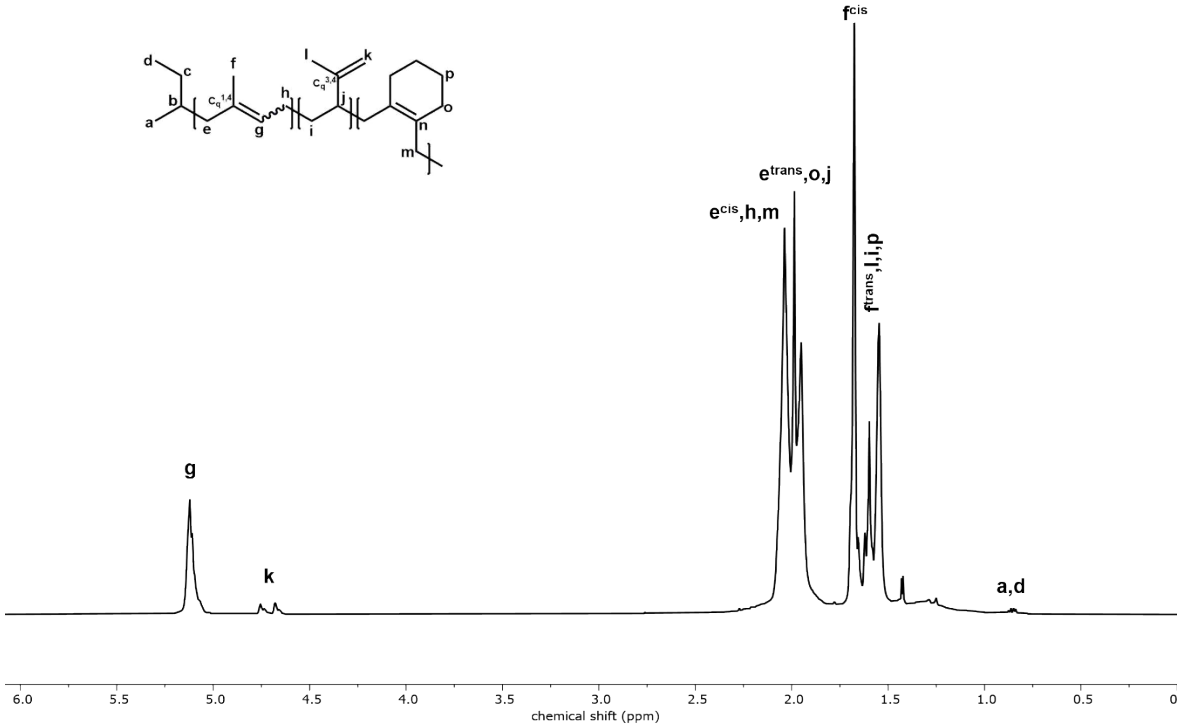



**Figure S27.** $^{1}$H-NMR spectrum (600 MHz, $CDCl_3$) of the polymer obtained by copolymerization of isoprene and DMCH in cyclohexane at 40 °C.

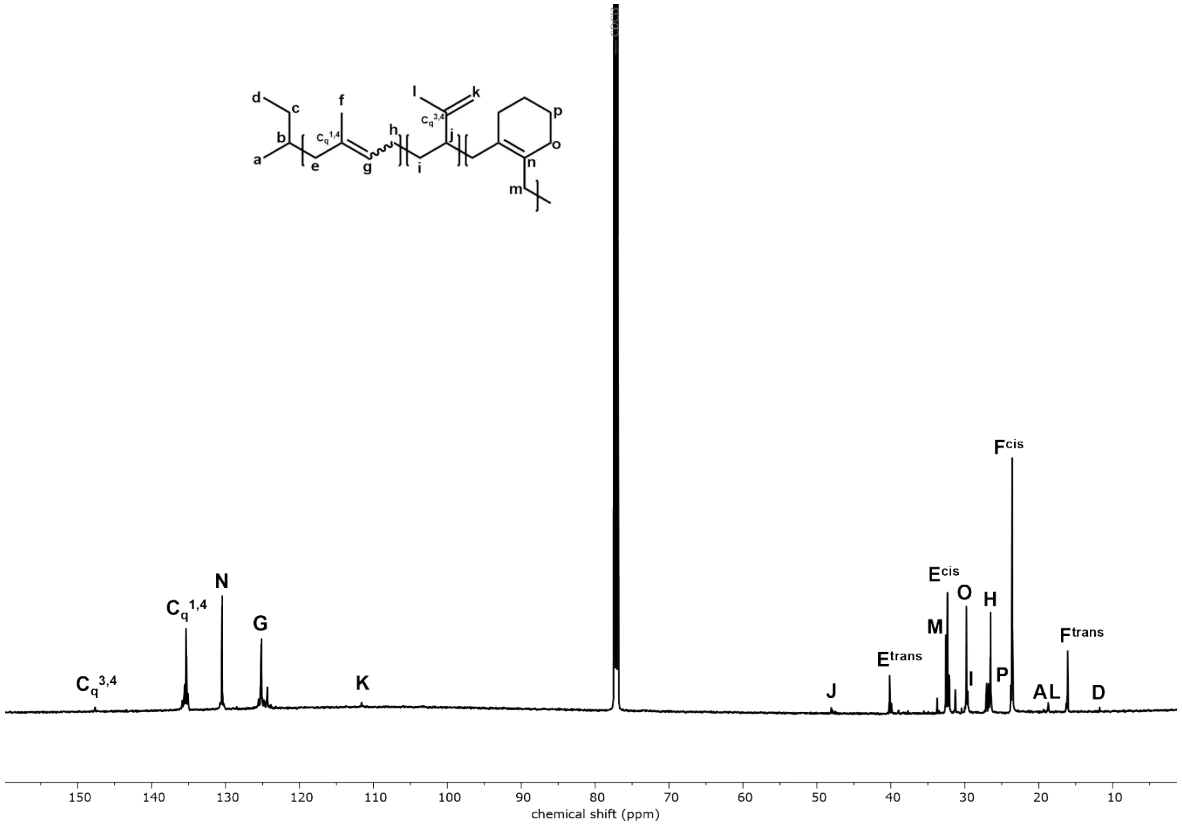



**Figure S28.** Inverse gated $^{13}$C-NMR spectrum (151 MHz, $CDCl_3$) of the polymer obtained by copolymerization of isoprene and DMCH in cyclohexane at 40 °C.

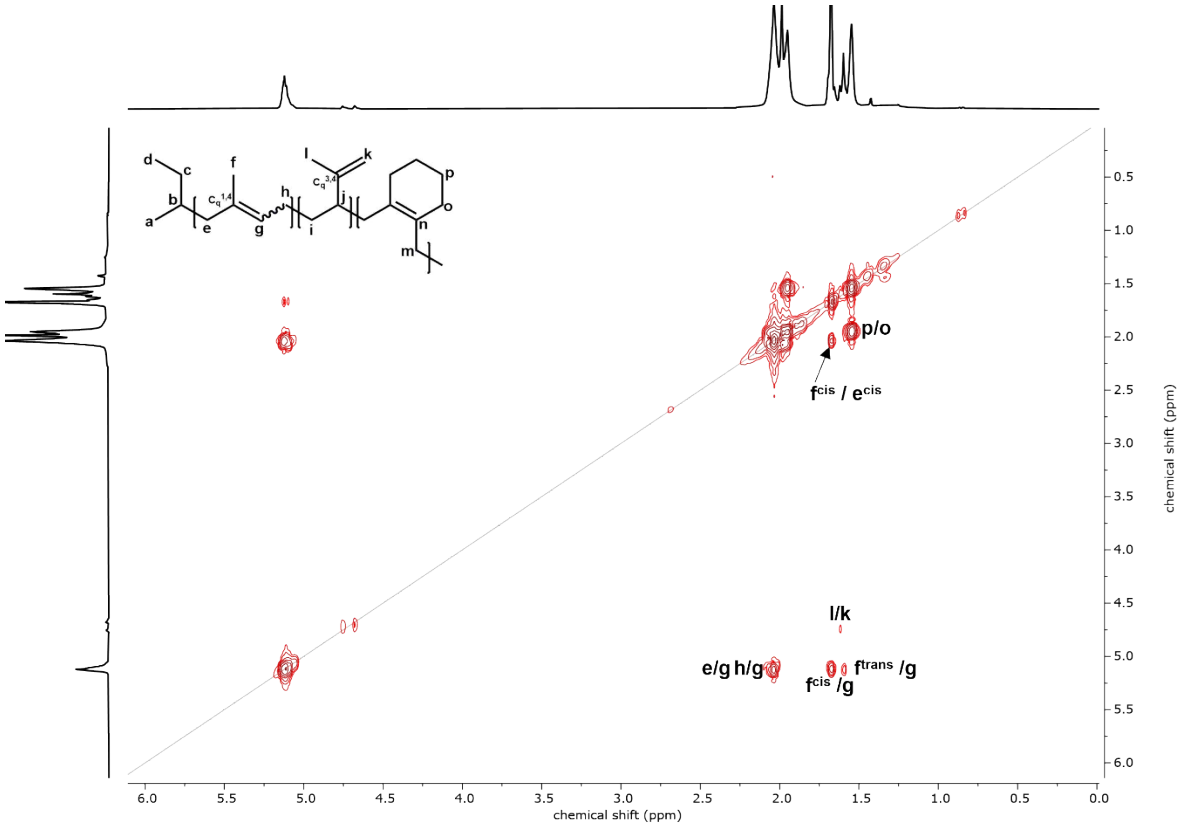



**Figure S29.** $^{1}H^{1}H$-COSY-NMR spectrum (600 MHz, $CDCl_3$) of the polymer obtained by copolymerization of isoprene and DMCH in cyclohexane at 40 °C.

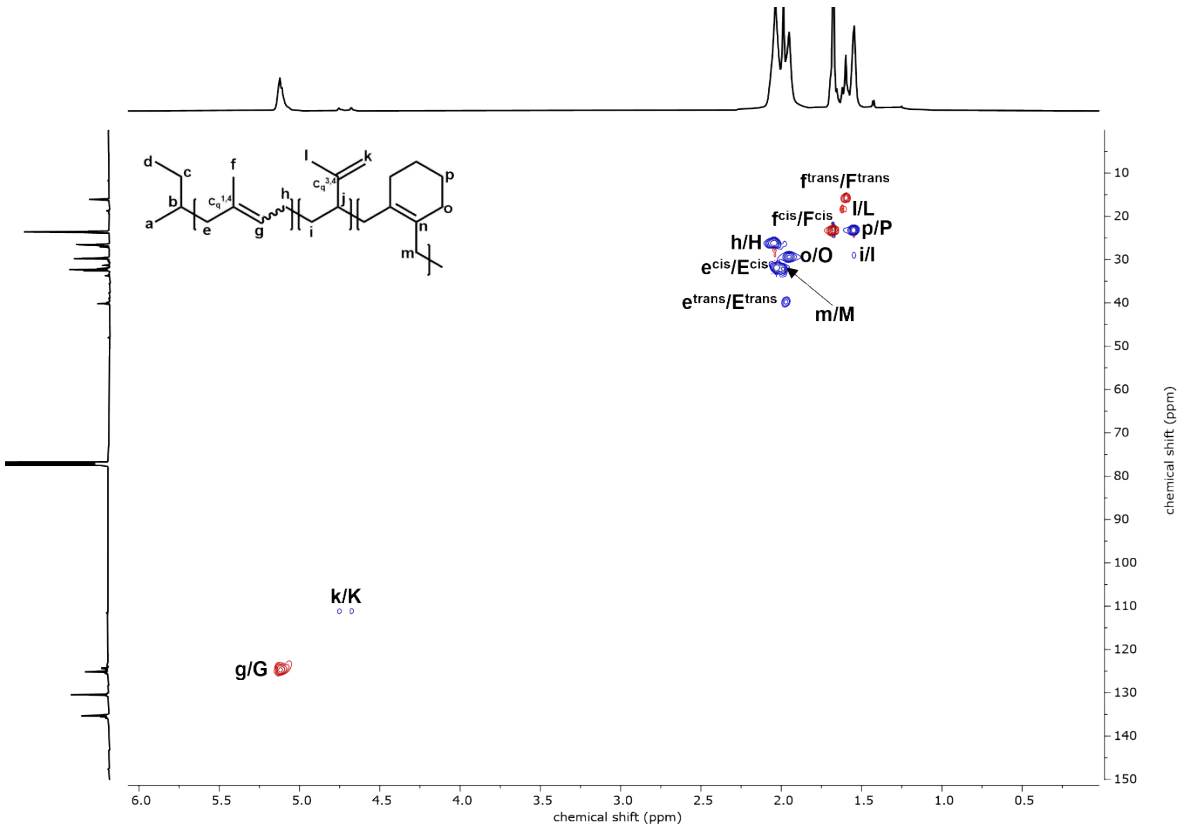



**Figure S30.** $^{1}H^{13}C$-HSQC-NMR spectrum (600/151 MHz, $CDCl_3$) of the polymer obtained by copolymerization of isoprene and DMCH in cyclohexane at 40 °C.

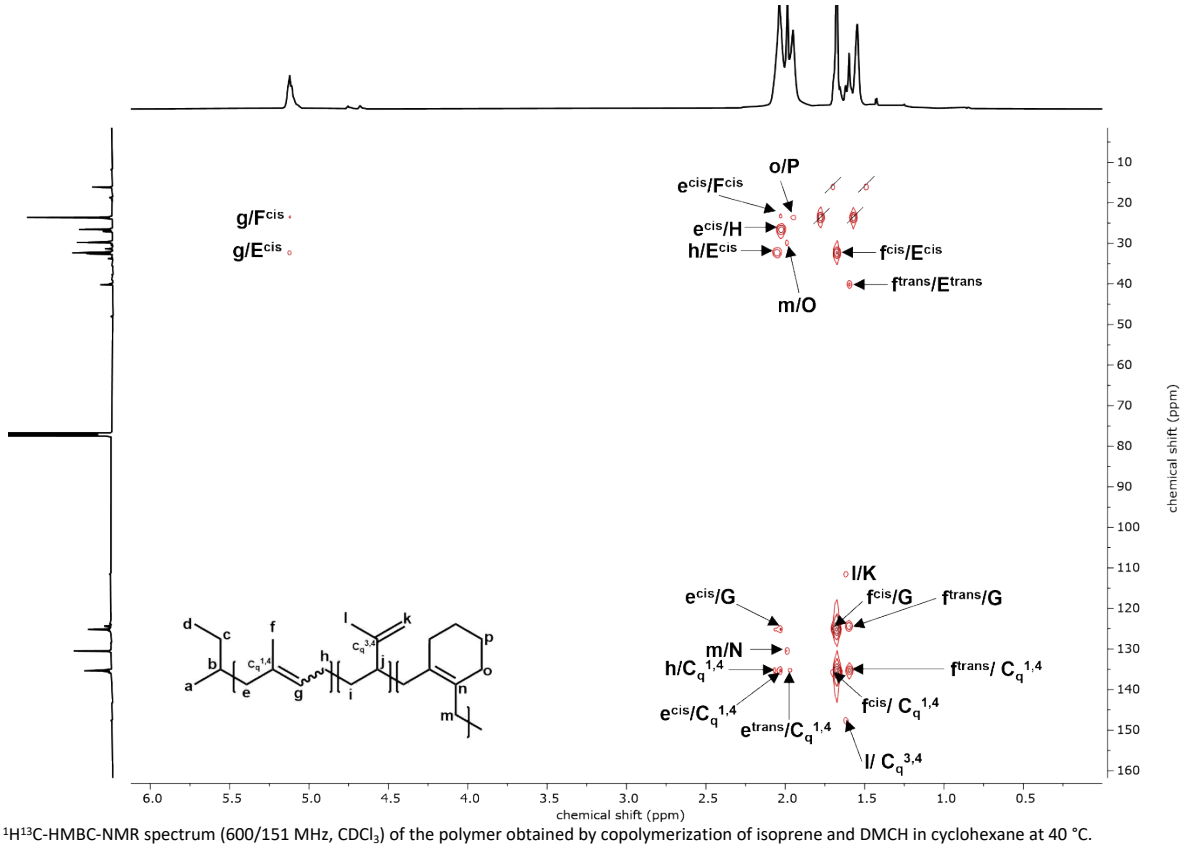



**Figure S31.** $^{1}H^{13}C$-HMBC-NMR spectrum (600/151 MHz, $CDCl_3$) of the polymer obtained by copolymerization of isoprene and DMCH in cyclohexane at 40 °C.

**MALDI-ToF spectra, SEC and NMR spectra of P(I-*co*-IMMCH)**

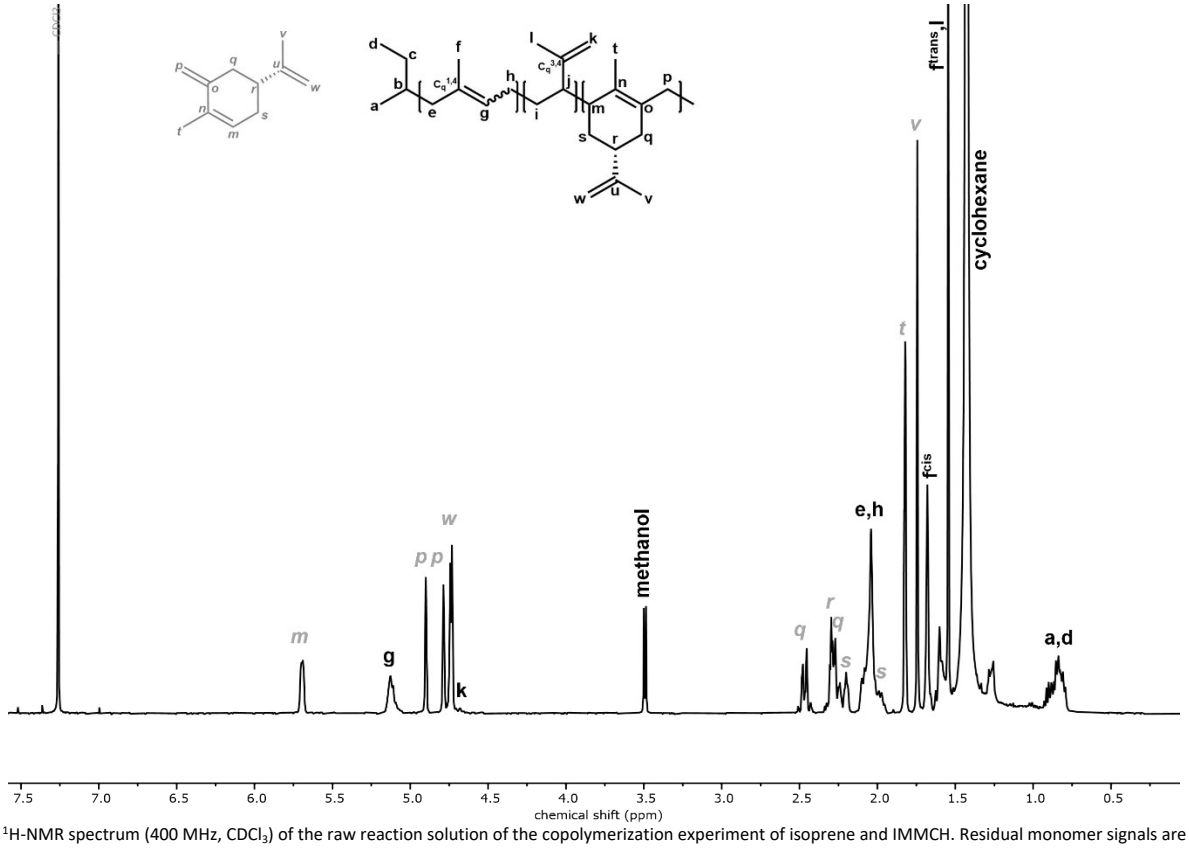



**Figure S32.** $^{1}$H-NMR spectrum (400 MHz, $CDCl_3$) of the raw reaction solution of the copolymerization experiment of isoprene and IMMCH. Residual monomer signals are assigned in italic and grey; polymer signals are denoted in black.

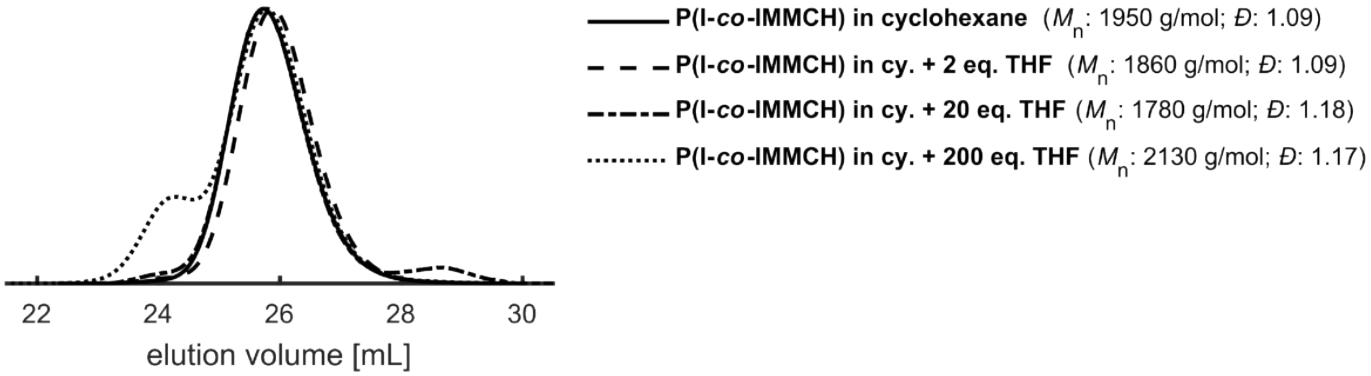



**Figure S33.** SEC traces (eluent: THF, detector: RI, calibration standard: PI) of the polymers obtained by copolymerization of isoprene and IMMCH in cyclohexane (black solid line), in cyclohexane with 2 equivalents of THF (black dashed line), in cyclohexane with 20 equivalents of THF (black dash-dotted line) and in cyclohexane with 200 equivalents of THF (black dotted line). Since 5000 g·mol$^{-1}$ and 50 mol% (~23 repeating units) of both isoprene and IMMCH were targeted, the observed molar masses together with the NMR and MALDI-ToF data show the consumption of all isoprene, but hardly no incorporation of IMMCH. The SEC trace of the polymer formed in the presence of 200 equivalents of THF shows multimodality, what could either be because of coupling in presence of oxygen during termination, or side reactions with THF. This could be the decomposition of THF by deprotonation at C2 and subsequent reverse [3+2] cycloaddition of the resulting anion, yielding ethylene and lithium enolate. Ethylene can react with alkyllithium compounds giving a saturated carbanionic chain end, while the enolate terminates the chain if it is added and beyond this can coordinate the lithium counterion strongly.

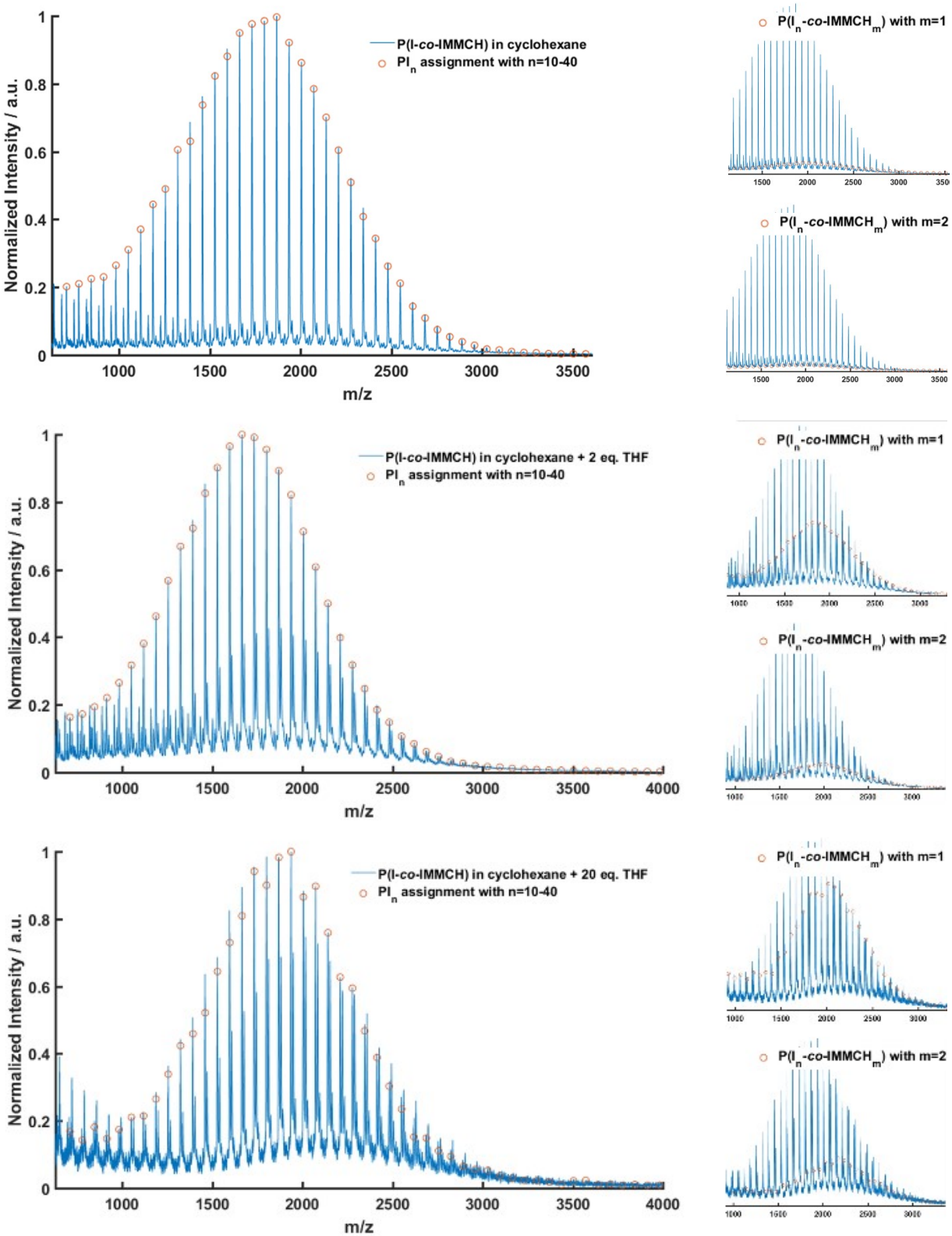



**Figure S34.** MALDI-ToF mass spectra of P(I-*co*-IMMCH) in cyclohexane with 0 (top), 2 (middle) or 20 (bottom) equivalents of THF. Matrix: DCTB, ionization agent: AgTFA, mode: linear. The distributions of pure polyisoprene $PI_n$ with n=10-40 are assigned in the main plot, while the distributions of polyisoprene with one or two IMMCH repeating units are marked In the cutouts on the right.

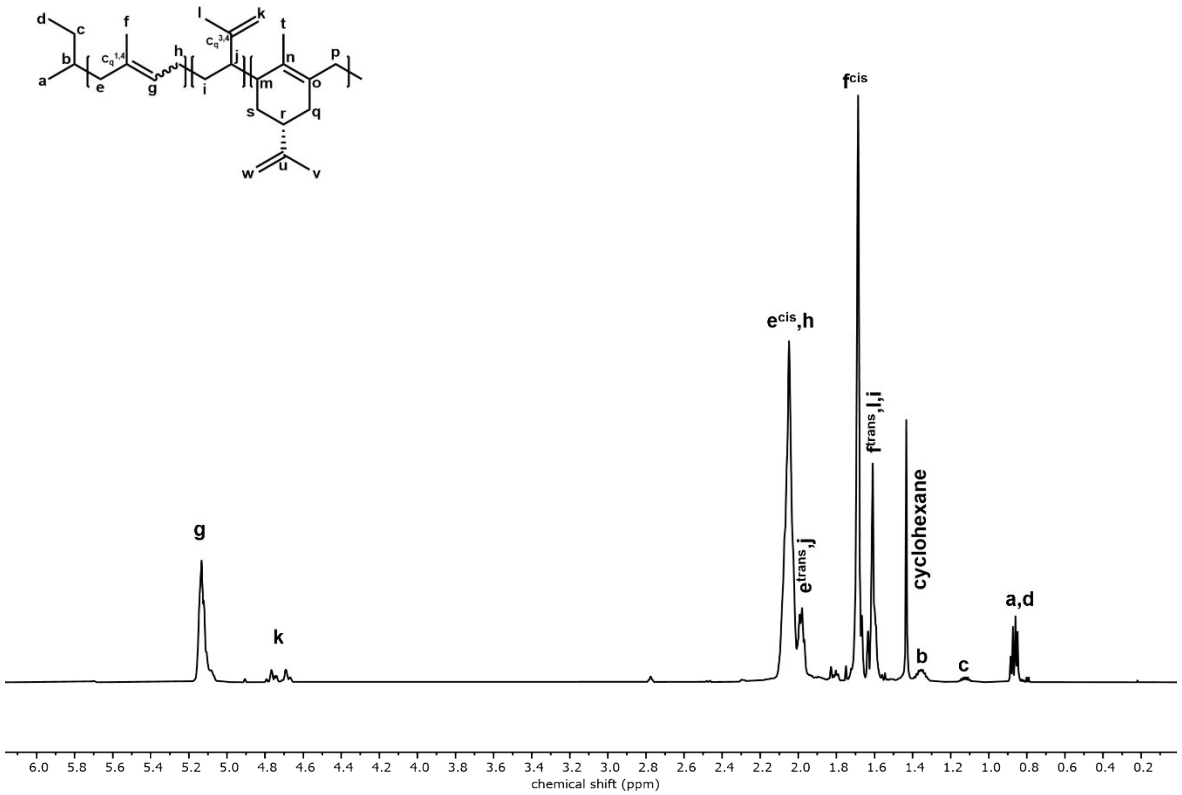



**Figure S35.** $^{1}$H-NMR spectrum (600 MHz, $CDCl_3$) of the polymer obtained by copolymerization of isoprene and IMMCH in cyclohexane. Only signals of PI are detectable.

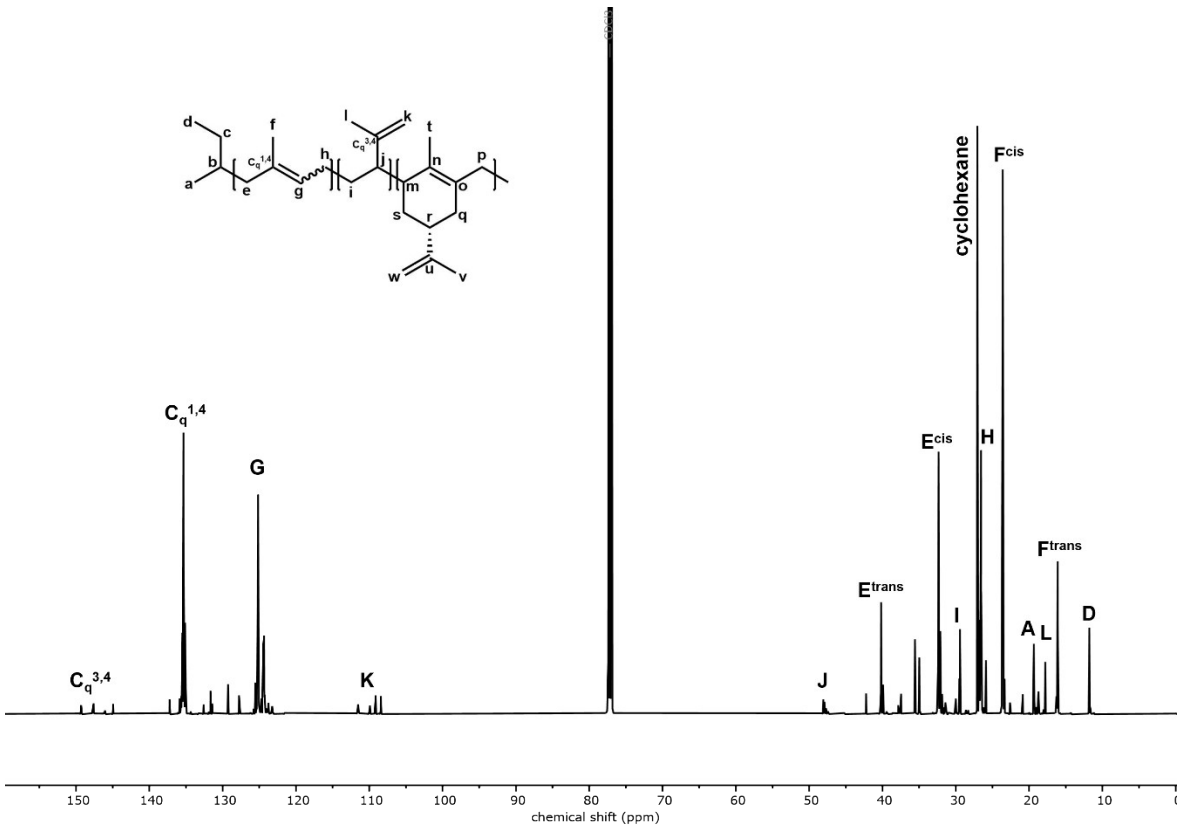



**Figure S36.** $^{13}$C-NMR spectrum (151 MHz, $CDCl_3$) of the polymer obtained by copolymerization of isoprene and IMMCH in cyclohexane. Only signals of PI are detectable.

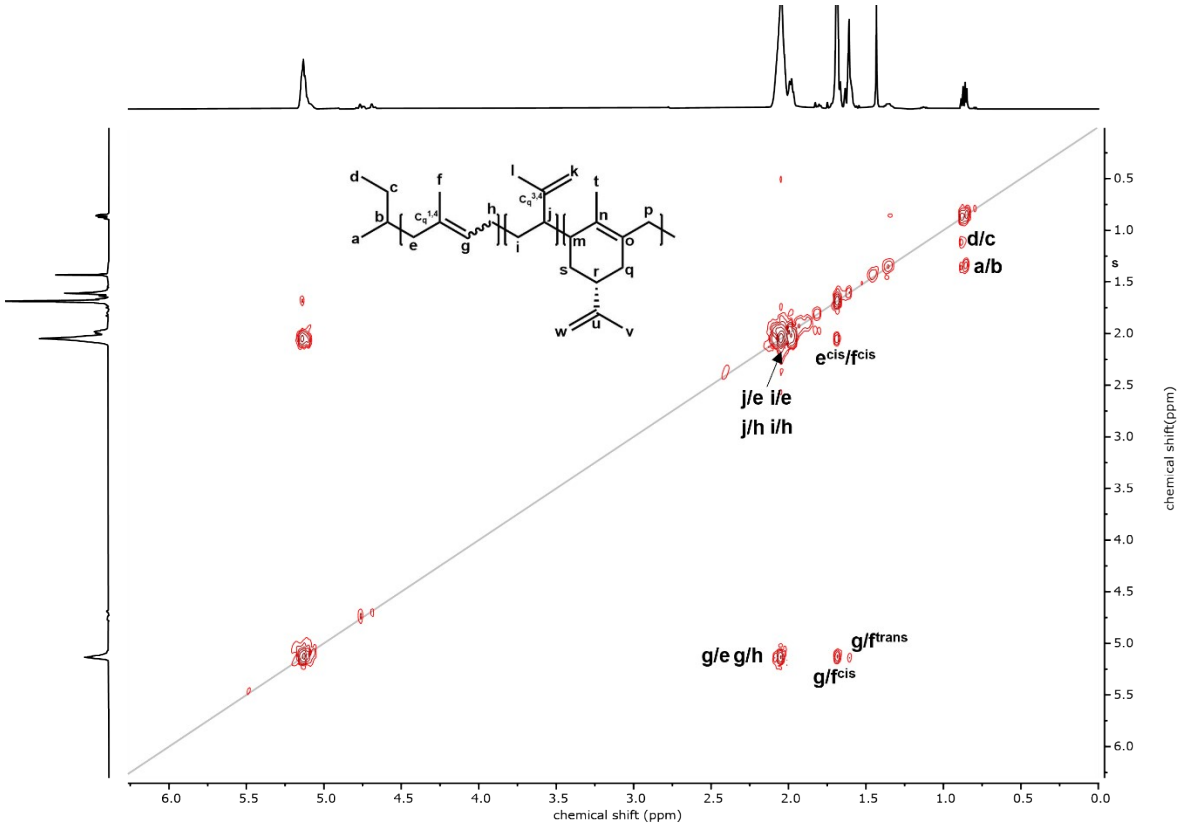



**Figure S37.** $^{1}H^{1}H$-COSY-NMR spectrum (600 MHz, $CDCl_3$) of the polymer obtained by copolymerization of isoprene and IMMCH in cyclohexane. Only signals of PI are detectable.

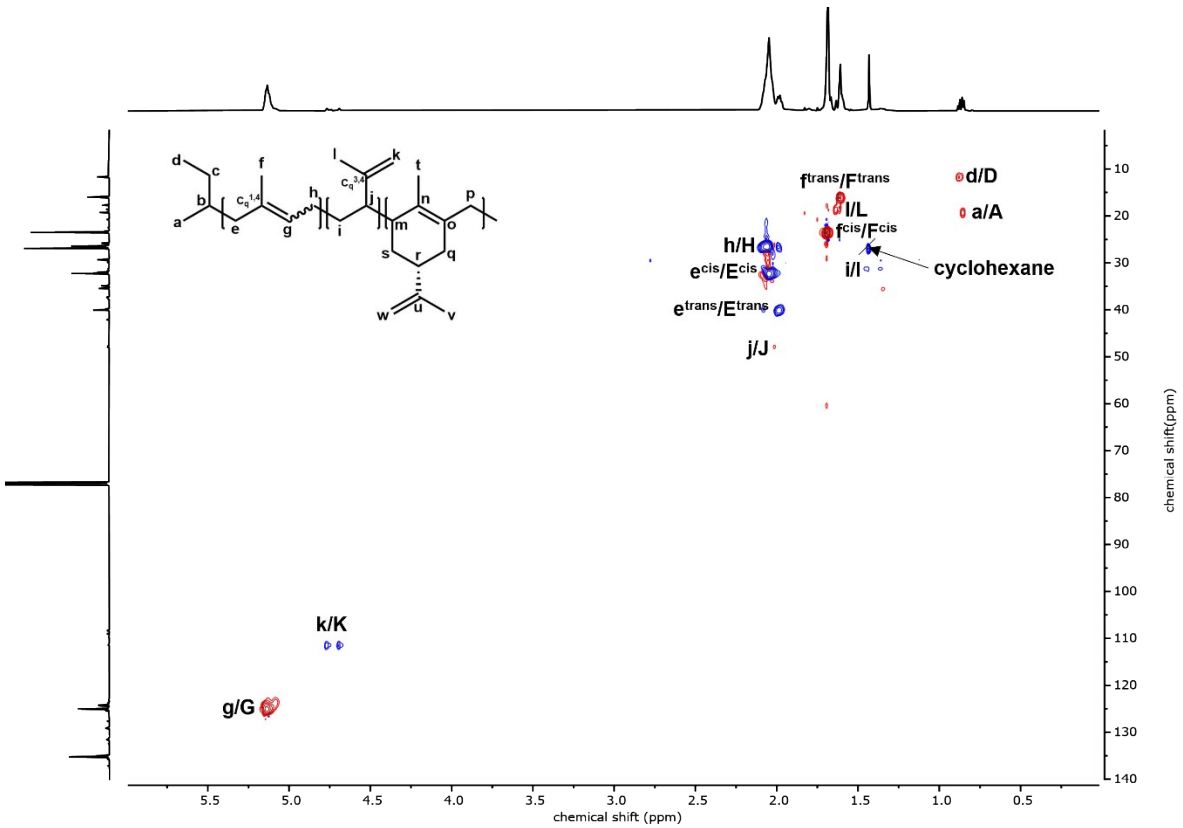



**Figure S38.** $^{1}H^{13}C$-HSQC-NMR spectrum (600/151 MHz, $CDCl_3$) of the polymer obtained by copolymerization of isoprene and IMMCH in cyclohexane. Only signals of PI are detectable.

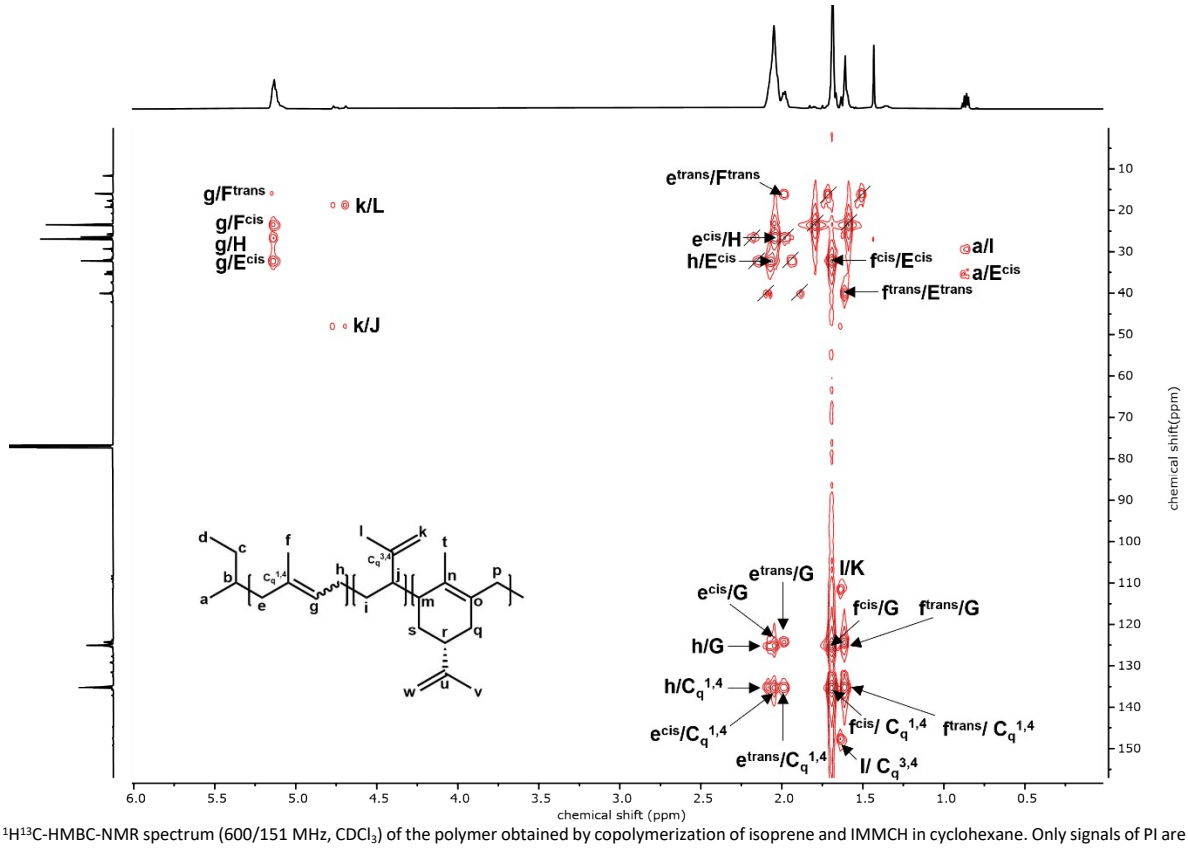



**Figure S39.** $^{1}H^{13}C$-HMBC-NMR spectrum (600/151 MHz, $CDCl_3$) of the polymer obtained by copolymerization of isoprene and IMMCH in cyclohexane. Only signals of PI are detectable.

1 M. E. Garst, L. J. Dolby, S. Esfandiari, R. A. Okrent and A. A. Avey, *J. Org. Chem.*, 2006, **71**, 553.