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Catalytic living ring-opening metathesis polymerization

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Experimental Section

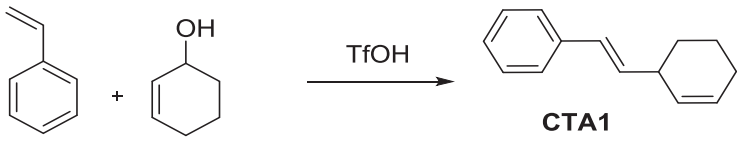
Materials:

Analytical grade solvents were purchased from Honeywell or Sigma-Aldrich and were used without further purification. Dry pyridine over molecular sieves was purchased from Sigma-Aldrich with the highest possible purity and used without further purification. Grubbs initiators **G1** and **G3**, dicyclopentadiene, ethyl vinyl ether were purchased from Sigma-Aldrich and used without further purification. Exo-*N*-methylnorbornene imide (**MNI**) was synthesized as reported previously (reference 16 in the main paper). 3A Molecular sieves were purchased from Sigma-Aldrich and activated at 100°C under vacuum for 24 hours before use. Deuterated solvents (CD_2Cl_2, $CDCl_3$) were purchased from Cambridge Isotope Laboratories, Inc. Deuterated dichloromethane was degassed by 3 successive freeze-vacuum-thaw cycles immediately before use.

Instrumentation:

ESI-MS analysis was carried out on a Bruker Daltonics Esquire HCT Mass Spectrometer with acetonitrile as the solvent. Matrix Assisted Laser Desorption Ionization Time of Flight (MALDI-ToF)-MS analyses of the polymers were carried out on a Bruker ultrafleXtreme™ using 2-[(2E)-3-(4-*tert*butylphenyl)-2-methylprop-2-enylidene]malononitrile (**DCTB**) as the matrix and silver trifluoroacetate as the ionizing salt. Relative molecular weights and molecular weight distributions were measured by gel permeation chromatography (GPC) at room temperature with chloroform as eluent and toluene as internal reference with a flow rate of 1 mL/min. GPC carried out on an instrument consisting of a Jasco PU-2087plus Pump and a set of two MZ-Gel SD*plus* linear columns (length x ID 300 x 8 mm; particle size 5µM) in series. Signal detection was performed With Applied Biosystems 759A Absorbance Detector (UV 254nm). The system was calibrated with polystyrene standards in a range from $10^3$to 3×10^6Da. NMR spectra were recorded on a Bruker Avance III 300 MHz NMR spectrometer (^{1}H-NMR 300 MHz; ^{13}C-NMR 75MHz). NMR signals were referenced internally to residual solvent signals. Ultra performance liquid chromatography / Mass spectrometry (UPLC-MS) analysis (LC-MS) was performed on a Waters UPLC® (H-Class Acquity) System equipped with a photodiode array detector (PDA), a SQ-detector (ESI & APCI Ionisation mode) and an ACQUITY UPLC® BEH C18 column (1.7 µm, 2.1 x50 mm). Inductively Coupled Plasma-Optical Emission Spectroscopy (ICP-OES) was done on a Perkin Elmer Optima 7000 DV ICP-OES instrument equipped with a CCD array detector, argon as the optical torch gas and nitrogen as the optical purge gas. The instrument was calibrated with solutions of Grubbs' first generation catalyst (**G1**) in dichloromethane. For the ICP-OES measurements, the polymers were dissolved in dichloromethane, diluted as appropriate. Results were processed in WinLab32 software.

Synthesis of CTA1:



CTA1

To a solution of cyclohex-2-en-1-ol (0.05 mol, 4.9 g, 1eq) and freshly distilled styrene (0.06 mol, 6.24 g, 1.2eq) in dibromoethane (100 mL) was added triflic acid (10 mol%). The mixture was heated at 65°C and stirred for 24 h. Upon completion of the reaction, the mixture was filtered through silica gel and washed with hexane to give a yellow solution. The solvent was removed by vacuum and the residue was purified by silica-gel flash column chromatography over a long column by using 100% hexane as the eluent. The product was isolated as a yellow liquid in 32% yield. However, the product contained some unreacted styrene and hence was distilled to give the pure product as a clear liquid.

^{1}H NMR (CHLOROFORM-d ,300MHz): δ 7.15 - 7.43 (m, 5 H), 6.34 - 6.46 (m, 1 H), 6.14 - 6.27 (m, 1 H), 5.80 (s, 1 H), 5.61 - 5.70 (m, J=2.3, 2.3, 2.3 Hz, 1 H), 2.96 (br. s., 1 H), 2.04 (tt, J=6.0, 3.0 Hz, 2 H), 1.84 - 1.95 (m, 1 H), 1.70 - 1.83 (m, 1 H), 1.46 - 1.68 ppm (m, 2 H). ^{13}C-NMR (CHLOROFORM-d ,75MHz): δ 137.8, 129.5, 129.0, 128.5, 128.1, 126.9, 126.0, 38.7, 29.3, 25.1, 20.5 ppm. ESI-MS ($C_{14}H_{16}$ + Na^{+}): Calculated: 184.28 Found: 184.28

Typical procedure for Catalytic Living Ring-Opening Metathesis Polymerization:

The catalyst (**G3,** 1equivalent), taken directly from the glove box in an argon atmosphere, was kept stirring in degassed dichloromethane in a Schlenk flask and the required amount of **CTA1** dissolved in degassed dichloromethane was added. Monomer (**MNI**) was purged free of oxygen by three cycles of alternating vacuum and argon atmosphere and dissolved in degassed dichloromethane. This monomer solution was taken up in a gas tight syringe and added at a rate of 0.5mL/hour. After complete addition, ethyl vinyl ether (100 equivalents) was added to quench any reactive metathesis species and the solution was poured in cold methanol to precipitate the polymer. The polymer was redissolved in DCM and reprecipitated once more, filtered, and dried under high vacuum.

G3 mg	G3 mmol	Monomer MNI mmol	CTA1 (with respect to G3)	CTA mmol	mon/CTA	Mn (GPC)	PDI
8.84	0.01	5.65	10eq	0.1	56.5	13380	1.06
8.84	0.01	5.65	20eq	0.2	28.3	7486	1.10
8.84	0.01	5.65	30eq	0.3	18.8	5024	1.12
8.84	0.01	5.65	40eq	0.4	14.1	3990	1.14
8.84	0.01	5.65	50eq	0.5	11.3	3280	1.15

Table 1: Table showing the amounts of **G3** used, amount of CTA used and the molecular weight analysis (by GPC) of the resultant polymers.

Analytical Section

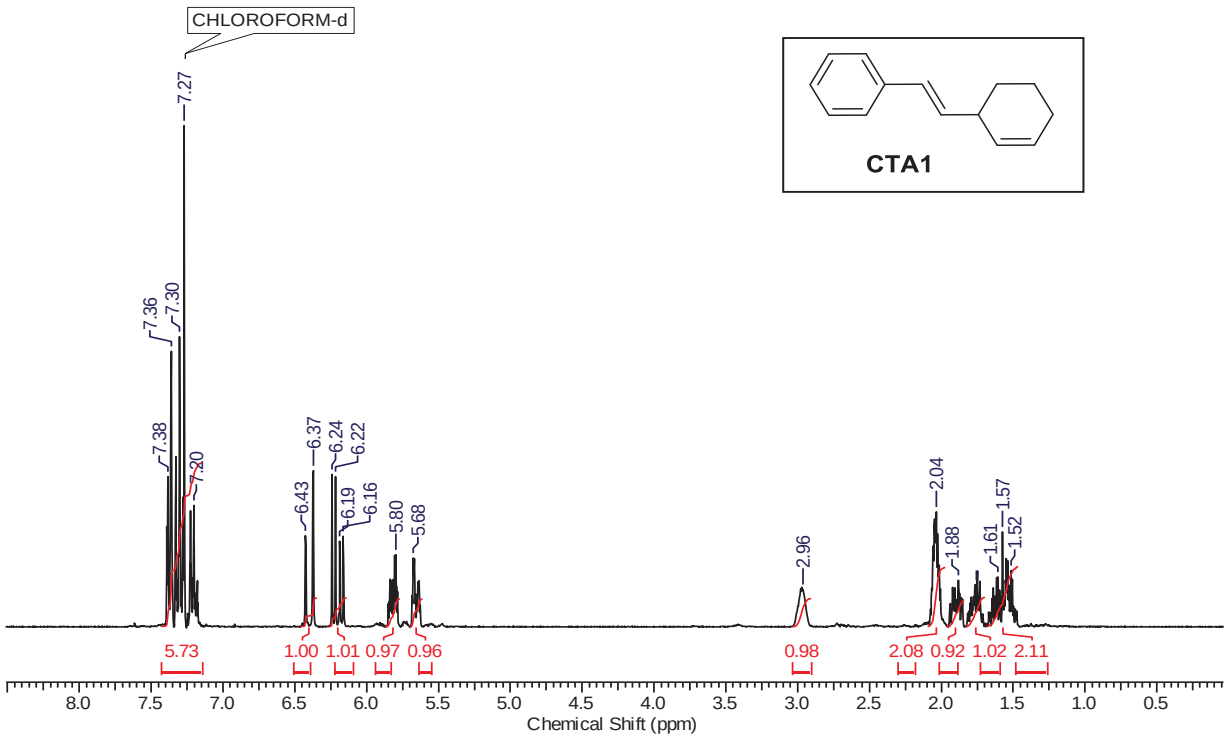


Figure 1: ^{1}H-NMR spectrum of **CTA1**

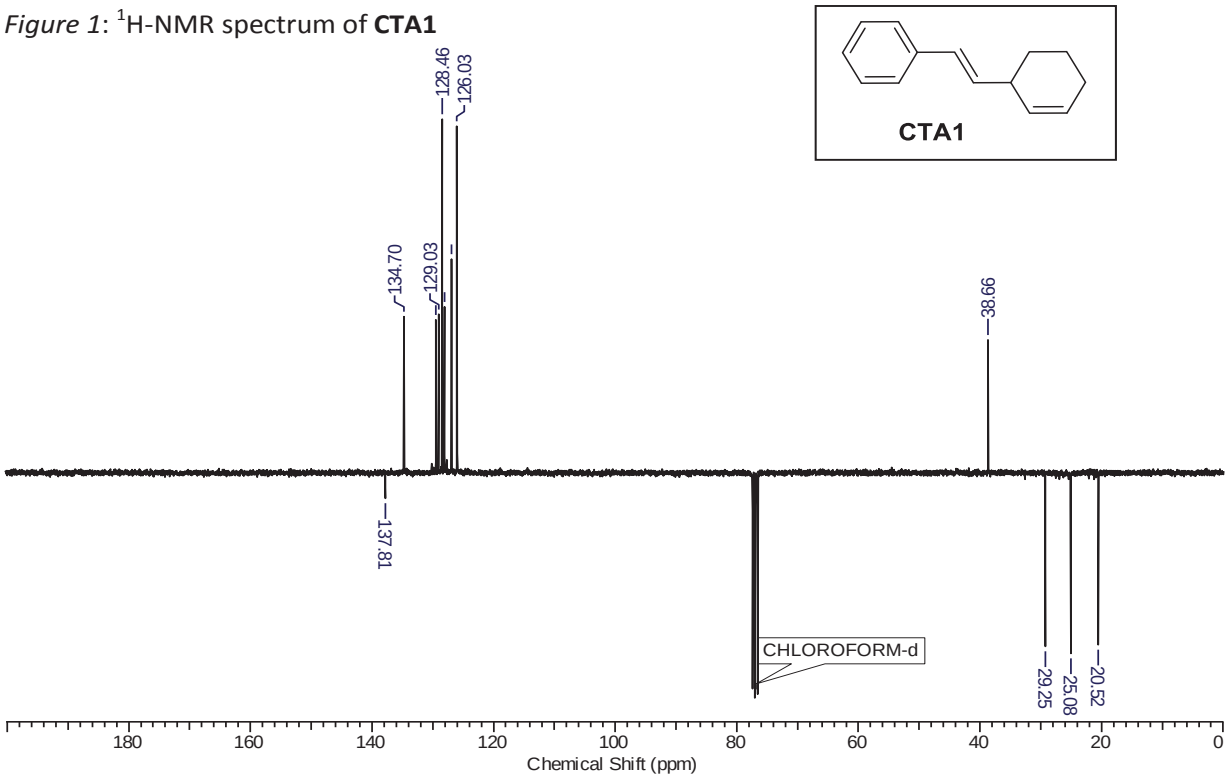


Figure 2: ^{13}C-APT NMR spectrum of **CTA1**

NMR Experiment for confirmation of non-polymerization of **CTA1**:

Grubbs' 3rd generation catalyst **G3** (8.84mg) was dissolved in degassed DCM-d2 and 50 equivalents of **CTA1** were added. The ^{1}H-NMR spectrum of the mixture revealed exclusively the characteristic **G3** peak in the carbene region (at 19.1ppm). No new olefins were observed in the ^{1}H-NMR spectrum. GPC analysis did not indicate any polymeric product. However, visually, the colour of the solution changed from dark green to brown, indicating an equilibrium reaction taking place, as shown below.

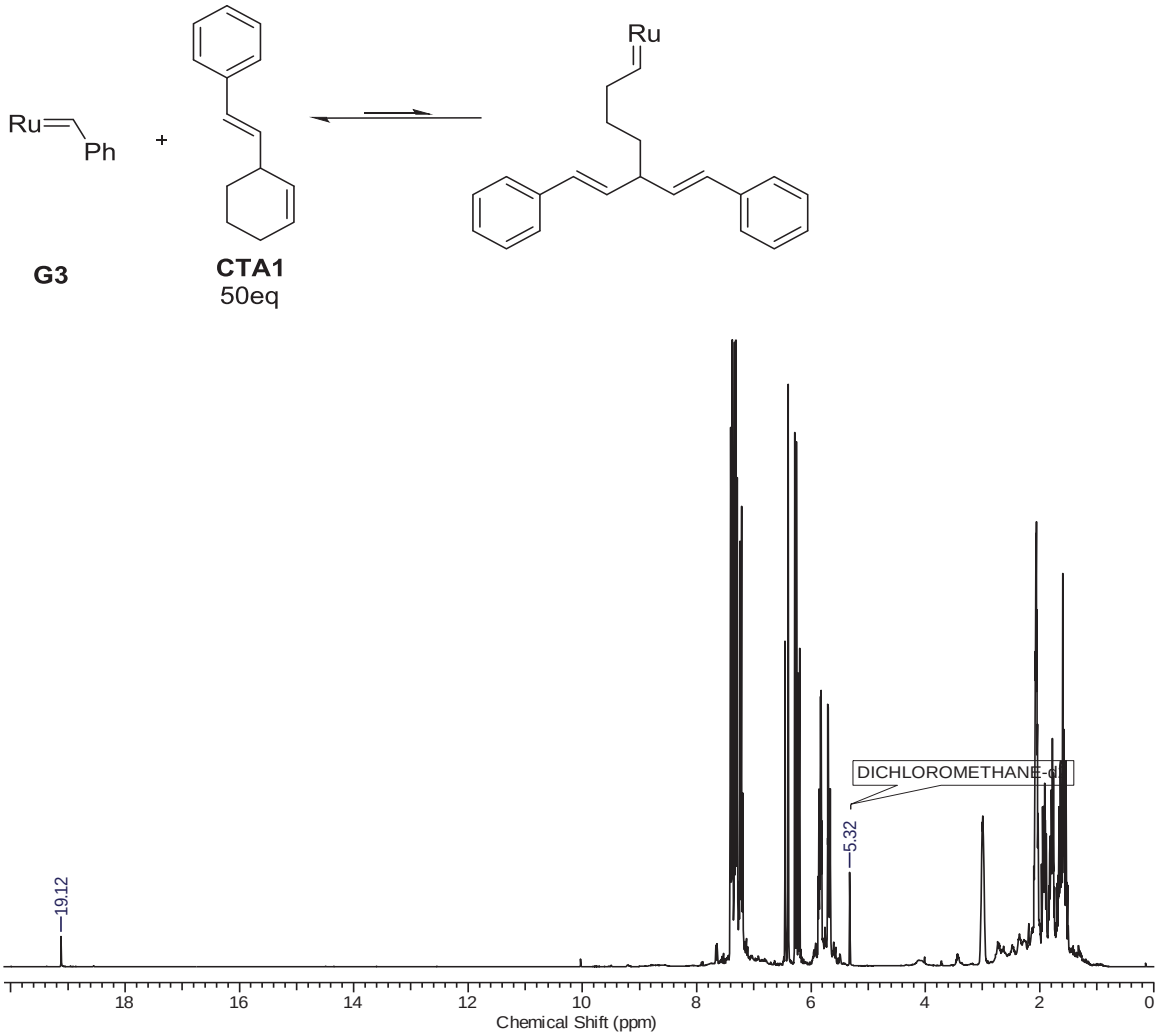


Figure 3: ^{1}H-NMR spectrum of the reaction mixture of **G3** with 50 equivalents of **CTA1**

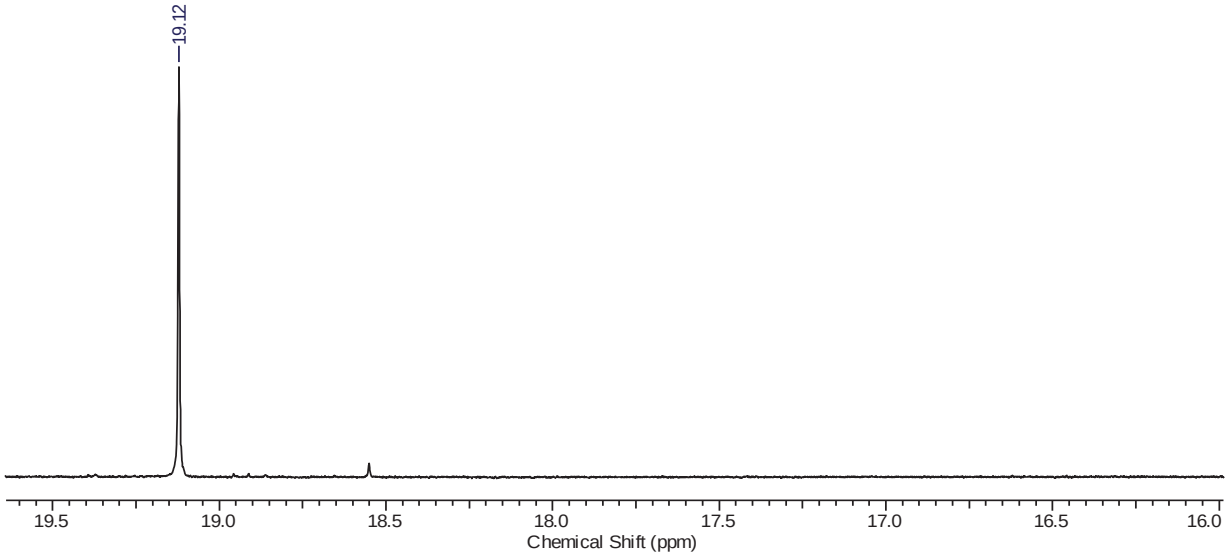
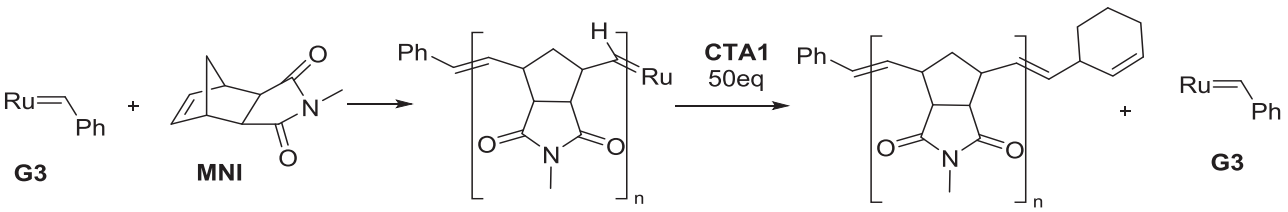


Figure 4: Magnified region of the carbene signals. An very small amount of a ruthenium alkylidene (at 18.56ppm) can be seen, which does not change even after 2 hours. This alkylidene could correspond to the open ruthenium alkylidene species described in Figure 3.

Regioselective End capping:



G3 (8.84mg, 0.01mmol, 1eq) was kept stirring in 0.2mL of DCM-d2 and the monomer **MNI** (30mg, 0.17mmol, 17eq) in 0.2mL of DCM-d2 was quickly added. This solution was transferred under argon into an NMR tube and a ^{1}H-NMR spectrum was measured (bottom NMR trace, black). To this NMR tube was added (37mg, 0.20mmol, 20eq) of **CTA1** and the ^{1}H-NMR spectrum was measured (top NMR trace, red).

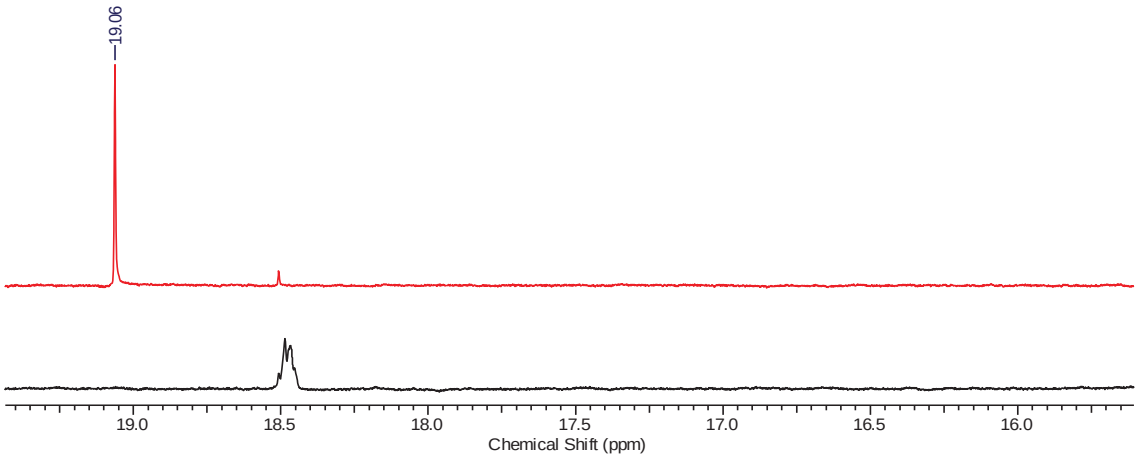


Figure 5: Superimposed ^{1}H-NMR spectra of the carbene region for proving the regioselective end capping.

As seen from the ^{1}H NMR data, the propagating ruthenium alkylidene at the polymer chain end shifts back to the original chemical shift of the benzylidene catalyst **G3**.

End-functionalization of the growing polymer chain with a cyclohexene end group:

When **G3** was reacted with 50eq of **CTA1** and then an excess (90 equivalents) of monomer **MNI** was quickly added, the ^{1}H-NMR spectrum showed the propagating alkylidene species at 18.5ppm which shifts back to the benzylidene species, proving the end functionalization of the growing polymer chain with a cyclohexene end group.

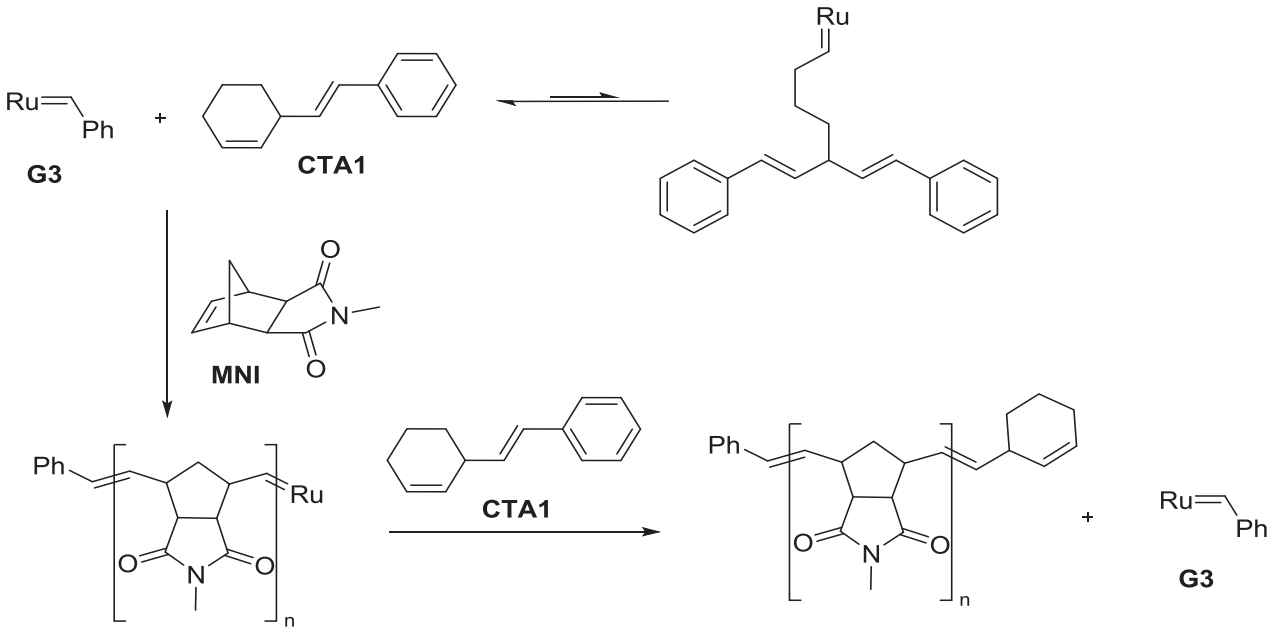


Figure 6: End-functionalization of the polymer chain by **CTA1**, regenerating the original benzylidene catalyst **G3**

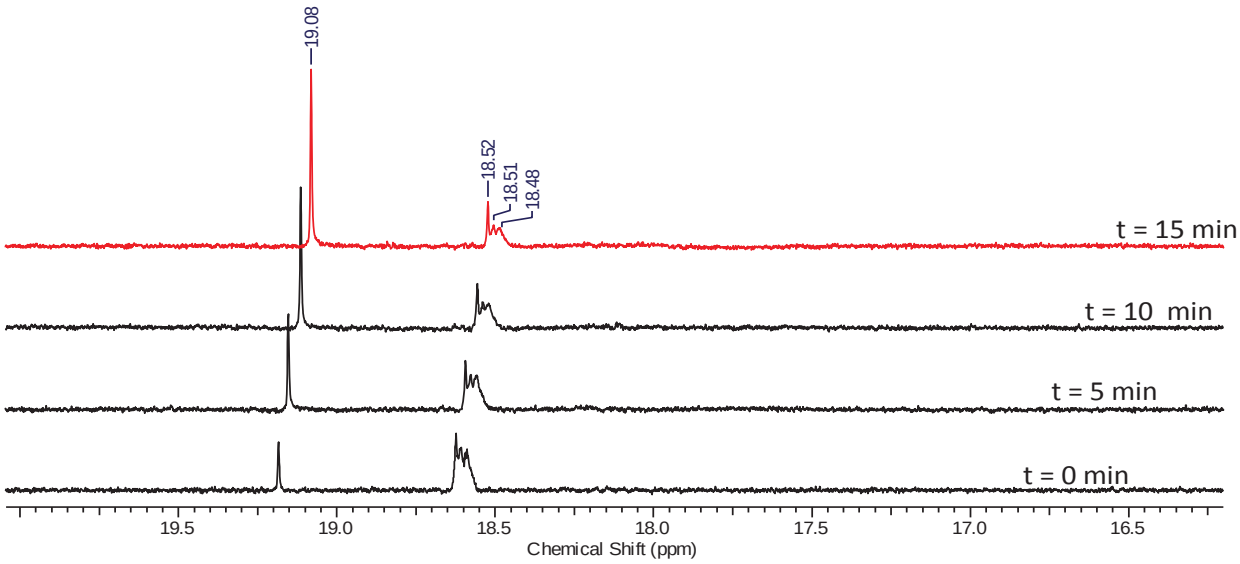


Figure 7: Time-resolved ^{1}H-NMR spectra of the end-functionalization of the polymer chain by **CTA1**, regenerating the original benzylidene catalyst **G3**. The alkylidene peak (at 18.5ppm) diminishes and the benzylidene peak (at 19.1ppm) grows back. The spectra are offset by 0.03ppm.

MALDI-ToF of the polymers:

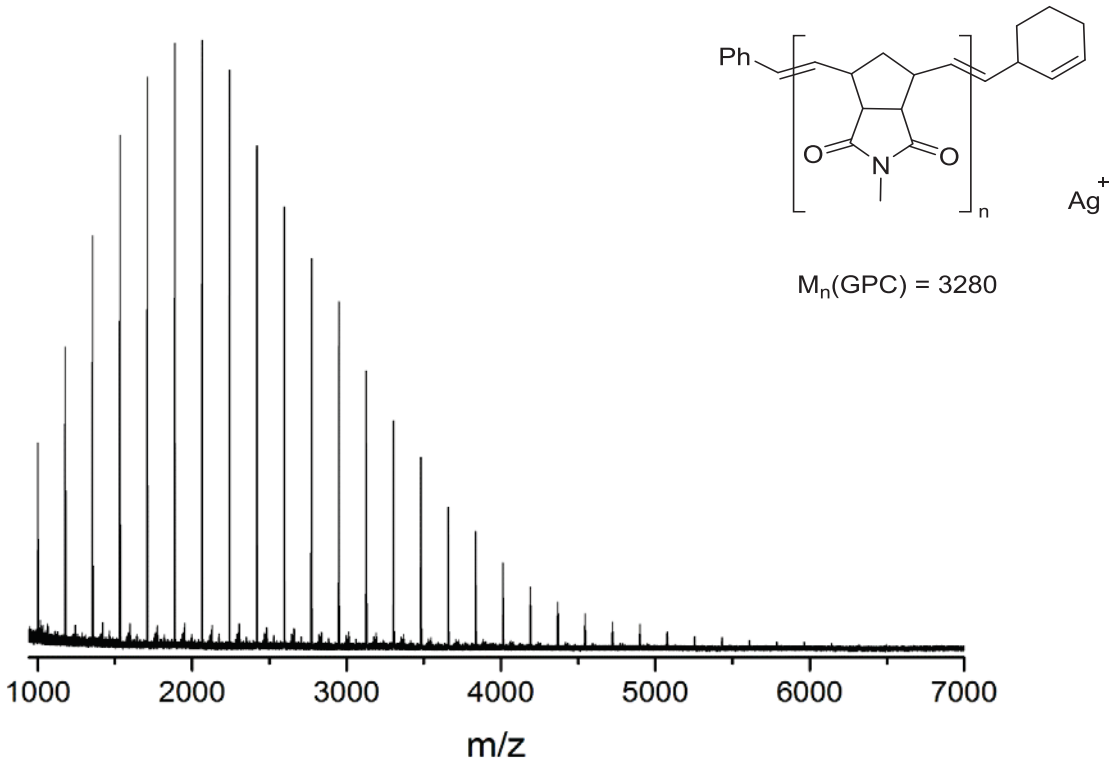


Figure 8: MALDI-ToF mass spectrum of the cyclohexyl end functional polymer (M_n=3280 by GPC).

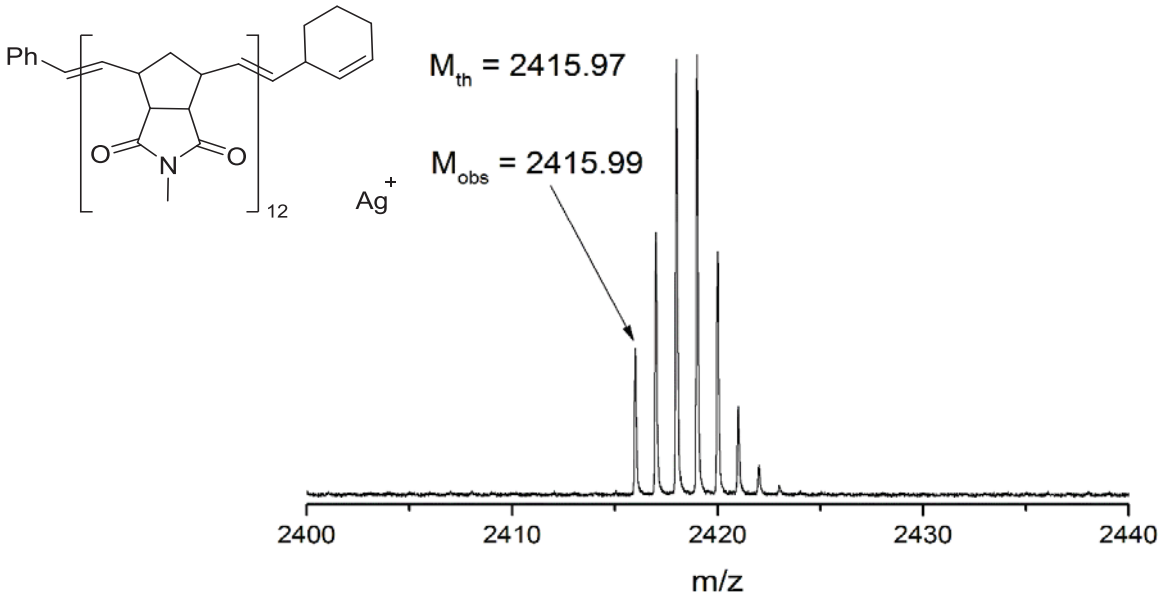
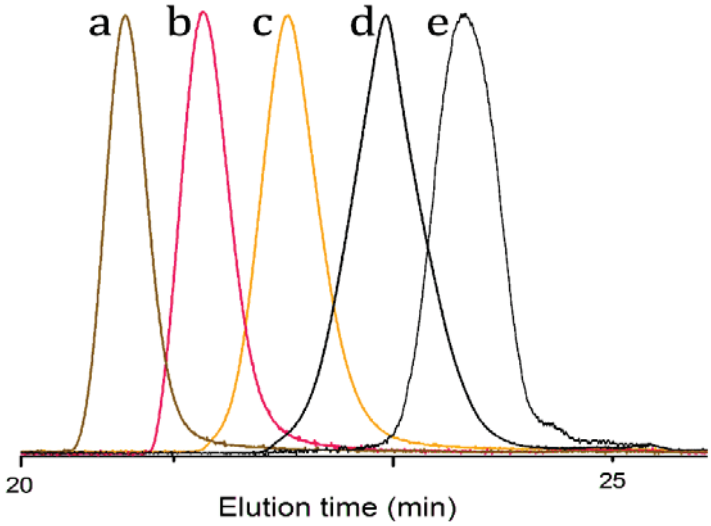


Figure 9: Enlarged MALDI-ToF mass spectrum of the cyclohexyl end functional polymer (M_n=3280 by GPC). The cyclohexyl end group is confirmed by the monoisotopic distribution.

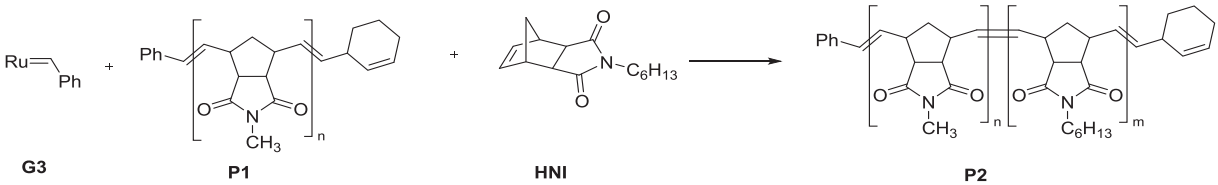
GPC data for the polymers:



GPC trace	Mn (GPC)	PDI
a	13380	1.06
b	7486	1.10
c	5024	1.12
d	3990	1.14
e	3280	1.15

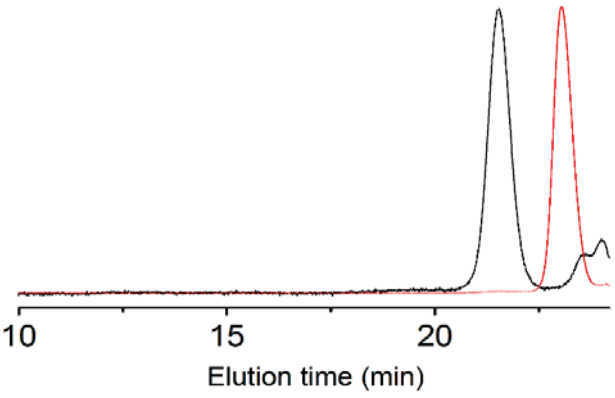
Figure 10: GPC traces of the polymers synthesized by the living catalytic ring opening metathesis polymerization process.

Block-copolymers experiment:



G3 P1 HNI P2

Polymer **P1** (300mg, Mn = 3280, c.a. 0.0914mmol) was kept stirring in dry degassed DCM and then **G3** (5mg, 0.056 mmol) in DCM was added. Monomer **HNI** (n-hexyl norborneneimide, 500mg, 1.62mmol) in 5mL DCM was added slowly via a syringe pump (0.5mL/hr). After complete addition, the polymerization was quenched with 0.2mL ethyl vinyl ether and the polymer was precipitated in cold methanol. GPC of this polymer showed a complete shift in the GPC of the new polymer **P2** as compared to polymer **P1**, proving the formation of block copolymers.



GPC trace	Mn (GPC)	PDI
black	9185	1.11
red	3280	1.15

Figure 11: GPC traces of polymer **P1** (red) and the block copolymer **P2** (black).

[1]H-NMR spectra of the polymers and end group analysis to determine the molecular weight.

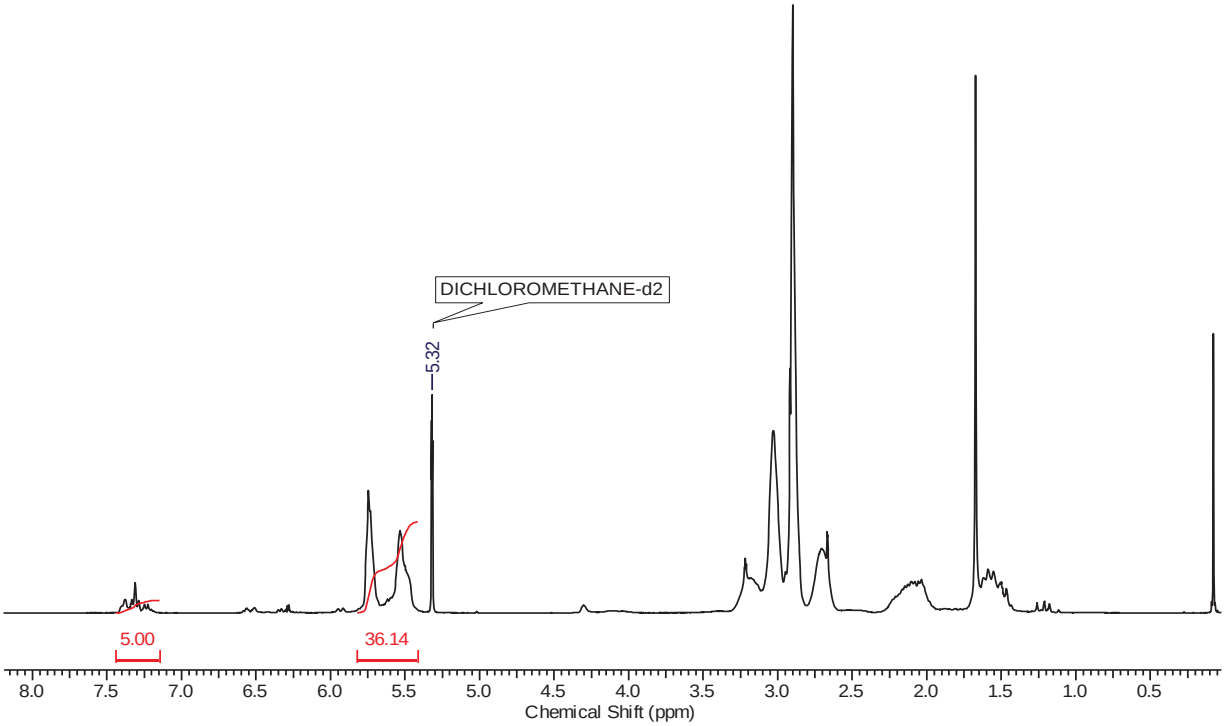


Figure 12: [1]H-NMR spectrum of the polymer obtained after polymerization in presence of 50eq of **CTA1** (Mn 3280)

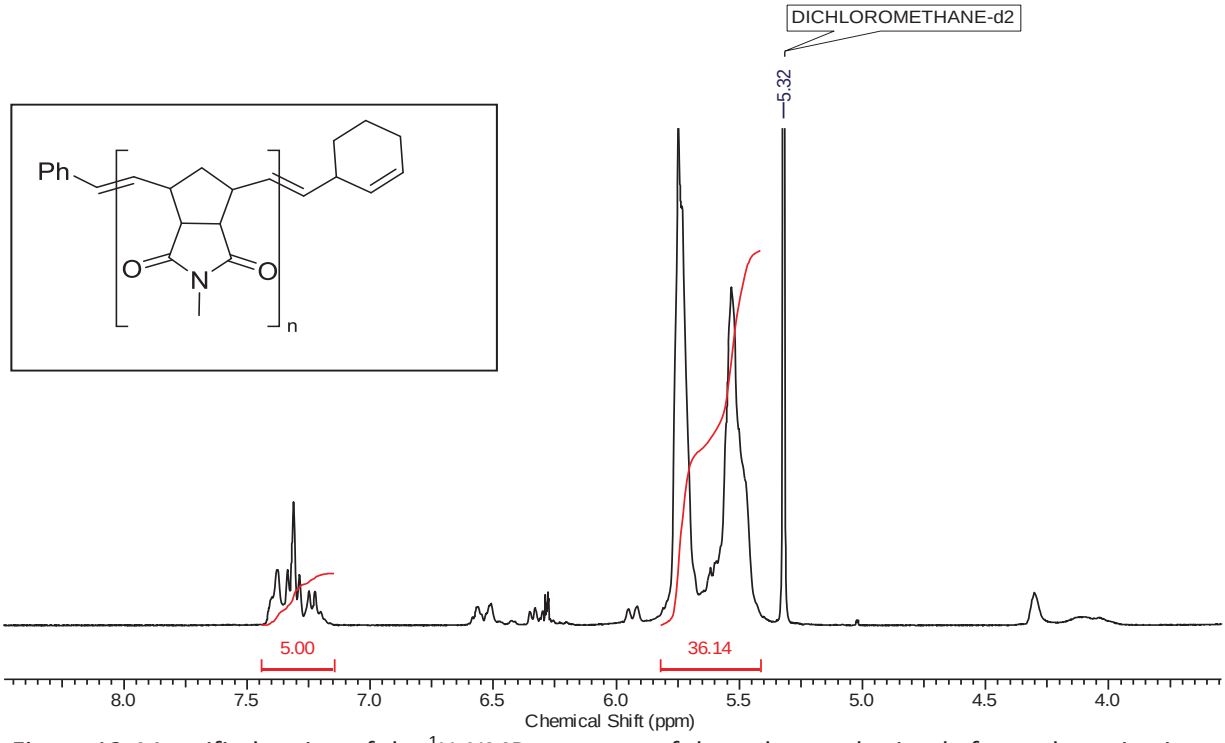


Figure 13: Magnified region of the [1]H-NMR spectrum of the polymer obtained after polymerization in presence of 50eq of **CTA1** (M_n = 3280).

The phenyl end group can clearly be seen and integrated with respect to the olefins in the polymer backbone. As two olefinic protons are present per monomer, the number of equivalents of the monomer is approximately (36-2)/2 = 17 (taking into consideration two olefinic protons of the end group). As the molecular weight of the monomer is 177, the polymer corresponds to a molecular weight of 17*177 = 3009 Da which is in good agreement with the molecular weight by GPC (Mn = 3280)

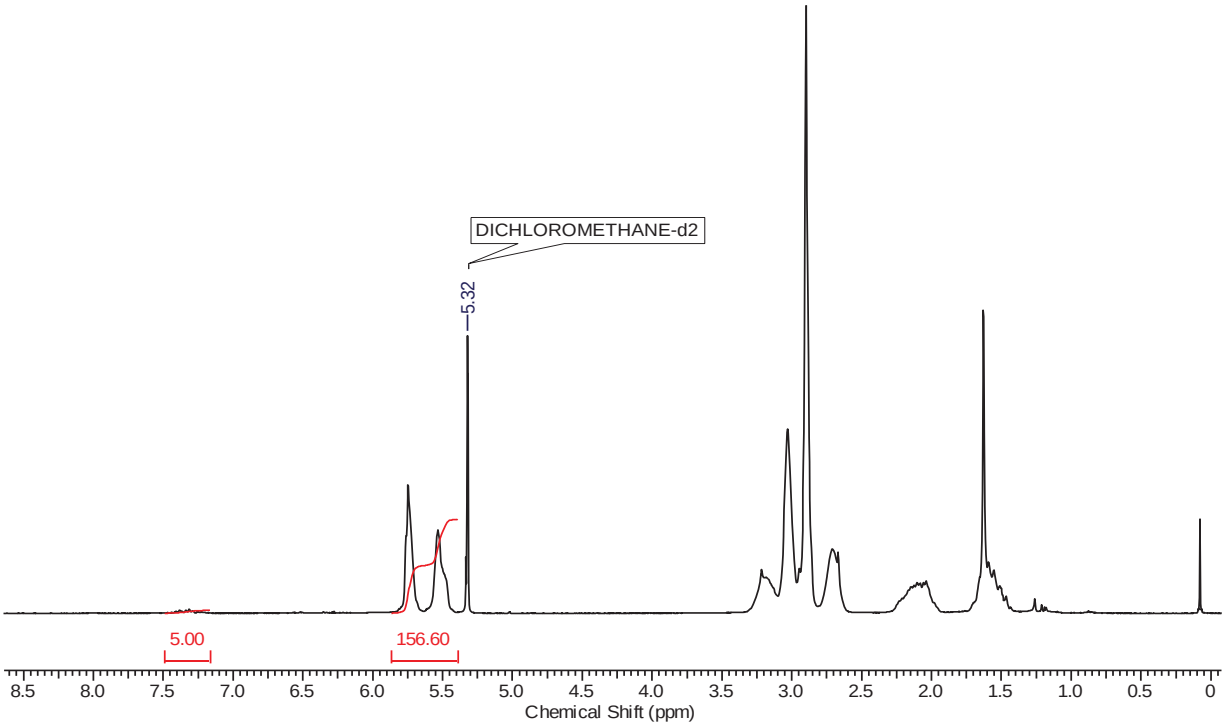


Figure 14: ^{1}H-NMR spectrum of the polymer obtained after polymerization in presence of 10eq of **CTA1** (M_n = 13380)

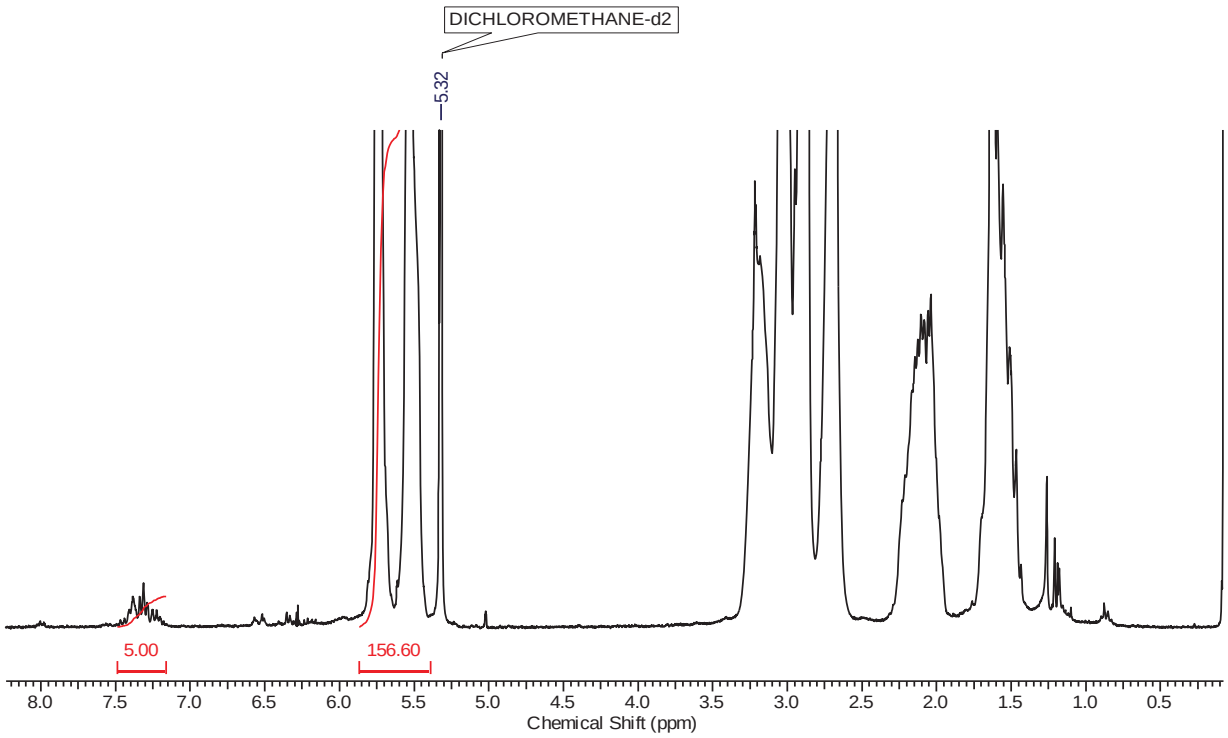


Figure 15: Magnified region of the ^{1}H-NMR spectrum of the polymer obtained after polymerization in presence of 10eq of **CTA1** (M_n = 13380).

Similar to the above NMR end group analysis, the polymer corresponds to a molecular weight of ((156-2)/2)*177 = 13629 Da which is in excellent agreement with the molecular weight by GPC (M_n = 13380)

Process	G3 mg	G3 mmol	Monomer MNI mmol	CTA1 (with respect to G3)	CTA mmol	mon/CTA	Mn (GPC)	PDI
catalytic ROMP	8.84	0.01	5.65	50eq	0.5	11.3	3280	1.15
ROMP	8.84	0.01	0.19	-	-	-	3440	1.08

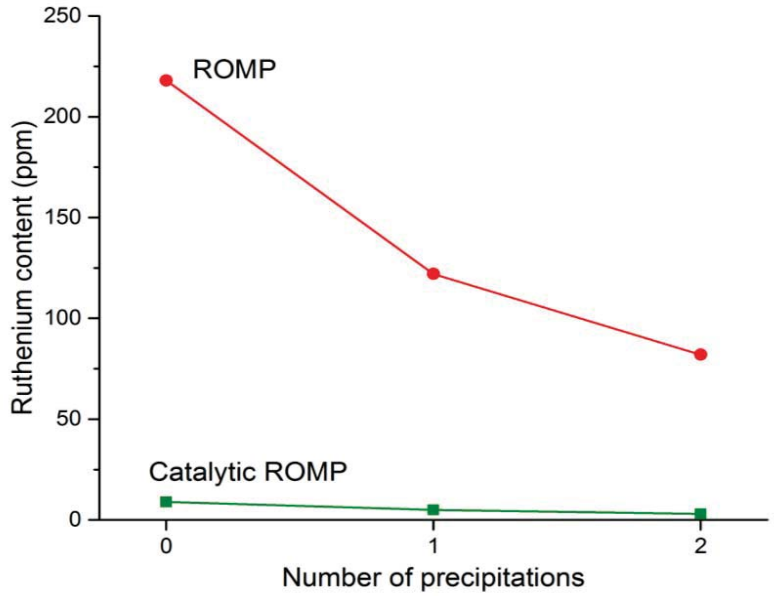


Figure 16: Residual ruthenium content by ICP-OES. Polymerization with 50 equivalents of **CTA1** by catalytic living ROMP vs. normal living ROMP of same monomer for similar molecular weight of the resulting polymers.

	Residual Ruthenium content ppm (mg/g)		
	Without ppt	1st ppt	2nd ppt
catalytic living ROMP	9	5	3
ROMP	218	122	82

Table 2: Comparison of the residual ruthenium content by ICP-OES (numbers rounded to the nearest integer).