Chemical Communications

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Supporting Information

for

High Molecular Weight Poly(*N*-methyl-2-vinylazaborine) – A Semi-Inorganic B-N Polystyrene Analogue

Birk Thiedemann,[a,b,c] Philipp J. Gliese,[a,b,c] Jonas Hoffmann,[c] Paul G. Lawrence,[d] Frank D. Sönnichsen*[c] and Anne Staubitz*[a,b,c]

a Institute for Organic and Analytical Chemistry, University of Bremen, Leobener Staße NW2c 28359 Bremen, Germany.

b MAPEX Center for Materials and Processes, University of Bremen, Bibliothekstraße 1, 28359 Bremen, Germany.

c Otto Diels Institute for Organic Chemistry, University of Kiel, Otto-Hahn-Platz 4, 24098 Kiel, Germany.

d School of Chemistry, University of Bristol, Cantock's Close, Bristol BS8 1TS, UK.

*fsoennichsen@oc.uni-kiel.de; *staubitz@uni-bremen.de*

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General Methods and Materials

All syntheses were carried out using standard Schlenk techniques or in a glovebox (INERT PURE LAB) under a dry and inert nitrogen atmosphere. Glassware and NMR-tubes were dried in an oven at 200 °C for at least 2 h prior to use. Reaction vessels were heated under vacuum und purged with nitrogen three times before adding reagents.

Analyses

^{1}H NMR, ^{13}C{^{1}H} NMR and ^{11}B NMR spectra were recorded at 300 K.

^{1}H NMR spectra were recorded on a Bruker DRX 500 (500 MHz) spectrometer or a Bruker AV 600 (600 MHz) spectrometer. Reaction monitoring was carried out on a Bruker DPX200 (200 MHz). ^{13}C{^{1}H} NMR spectra were recorded on a Bruker DRX 500 (500 MHz) spectrometer or a Bruker AV 600 (126 MHz) spectrometer. ^{11}B NMR spectra were recorded on a Bruker DRX 500 (160.46 MHz) spectrometer with 2048 scans, and a spectral width of 40000 Hz (250 ppm), a relaxation delay of 0.15 s, and an acquisitions delay of 0.1 s. The signals were referenced externally to $BF_3{\cdot}OEt_2$.

The exact assignment of the peaks was proved by ^{1}H, ^{13}C{^{1}H} DEPT and two-dimensional NMR spectroscopy such as ^{1}H COSY, ^{13}C HSQC(-DEPT) or ^{1}H/^{13}C HMBC when possible.

IR spectra were recorded on a Perkin Elmer Paragon 1000 FT-IR spectrometer with an A531-G Golden-Gate-ATR-unit.

The high resolution EI mass spectra were measured on a VG Analytical Autospec apparatus.

Thermogravimetric analyses (TGA) were conducted on a Mettler Toledo TGA/DSC 3+ Star^{e} System.

Differential scanning calorimetry (DSC) measurements were conducted on a Mettler Toledo DSC 3+ Star^{e} System.

For Gel permeation chromatography (GPC) measurements, a PSS GPC/SEC System equipped with three separation columns (1.000 Å, 100.000 Å and 1.000.000 Å), a RI detector, viscometer (DVD1260) and diode array detector (DAD1260).

All microwave irradiation reactions were carried out on a Biotage Initiator 60EXP.

Chemicals

All reagents were degassed via the freeze-pump-thaw technique (>3 cycles), dried and stored under a N_2 atmosphere, if not mentioned otherwise.

Compound	Purity	Comment
2,2′-Azobis(2-methylpropionitrile)	98%	Sigma Aldrich; dried under vacuum and flushed with N_2 (3 times before transferring

		into the glovebox)
2-Vinyltoluene (or 2-Methylstyrene)	>95%	Sigma Aldrich; 3x FPT
BCl_3, Boron trichloride	1.0 M in hexanes	Acros Organics; not degassed
Cyclohexene	99%	inhibitor-free; dried over molecular sieves (3 Å)
Grubbs Catalyst 1st Generation	97%	Sigma Aldrich; degassed under vacuum for 16 h
Magnesium turnings	Technical, special for Grignard reactions	Fisher Scientific/Acros
n-BuLi, *n*-buthyllithium	2.5 M in hexanes	Acros Organics, not degassed
N-Methylallylamine	96%	Alfa Aesar; dried over molecular sieves (3 Å)
Pd black, Palladium black	99.9%	ABCR; degassed under vacuum for 16 h
Tetravinylstannane	95%	Acros Organics; dried over molecular sieve (3 Å)
Triethyl amine, Et_3N	99%	Grüssing; dried over molecular sieve (3 Å)

Solvents

All solvents were used after purification as described below (Table SI- 1). Dried solvents were regularly tested for water content by Karl Fischer titration. In all syntheses and work-up procedures exclusively dried and degassed solvents were used. SPS = Solvent purification system (PureSolv from INERT TECHNOLOGY).

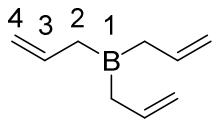
Table SI- 1. Purification of solvents.

Solvent	Drying procedure	Water content
CH_2Cl_2	Directly used from the SPS (columns: 2x aluminium oxide)	< 5 ppm
Et_2O	Predried over KOH; dried and distilled over sodium and stored over molecular sieves (3 Å)	< 5 ppm
n-Pentane	Obtained from the SPS (columns: 1x aluminium oxide, 1x copper(I) oxide and degassed 3 times by the freeze-pump-thaw technique	< 5 ppm
Toluene	Directly used from the SPS (columns: 1x molecular sieve, 1x aluminium oxide)	< 5 ppm

Syntheses

Monomer Synthesis and Characterization

Triallylborane[1]



According to Brown and Racherla:[1]

A dried two neck flask equipped with a reflux condenser (connected to Schlenk line) and a septum with connection to a syringe pump was placed under a nitrogen atmosphere. This apparatus was filled with dry magnesium turnings (9.73 g, 400 mmol), anhydrous and degassed diethyl ether (300 mL) and BF_3 etherate (12.4 mL, 100 mmol). Dried and degassed allyl bromide (26 mL, 300 mmol) was added via a syringe pump over the course of 3 h. After addition, the mixture was stirred for a further 12 h. Then insoluble magnesium salts were allowed to settle by switching off the stirrer. The clear ether layer was transferred via a PTFE tube into a dried two-neck Schlenk flask, which was connected to a distillation apparatus. The magnesium salts were washed with anhydrous and degassed diethyl ether (2 x 80 mL). The diethyl ether layers were combined. Solvent and potentially remaining starting material were stepwise removed (50-60 °C; atm pressure N_2 until 200 mbar). Finally, a short-path distillation (70 °C; 15 mbar) resulted in triallylborane (8.64 g, 64.5 mmol, 64%).[a,b] ^{1}H NMR (500 MHz, C_6D_6) δ 5.81 (3 H, dt, J = 21.2, 10.5, 10.5 Hz, 3-H), 4.94 (6 H, m, 4-H), 2.03 (6 H, m, 2-H); ^{13}C{^{1}H} NMR (126 MHz, C_6D_6) δ 135.2 (C-3)114.9 (C-4), 34.8 (C-2); ^{11}B NMR (161 MHz, C_6D_6) δ 81.1.

[a] With our available equipment, IR spectroscopy cannot be performed for air sensitive compounds.
[b] High resolution mass spectrometry showed both no mass signal and no identifiable fragment signal.

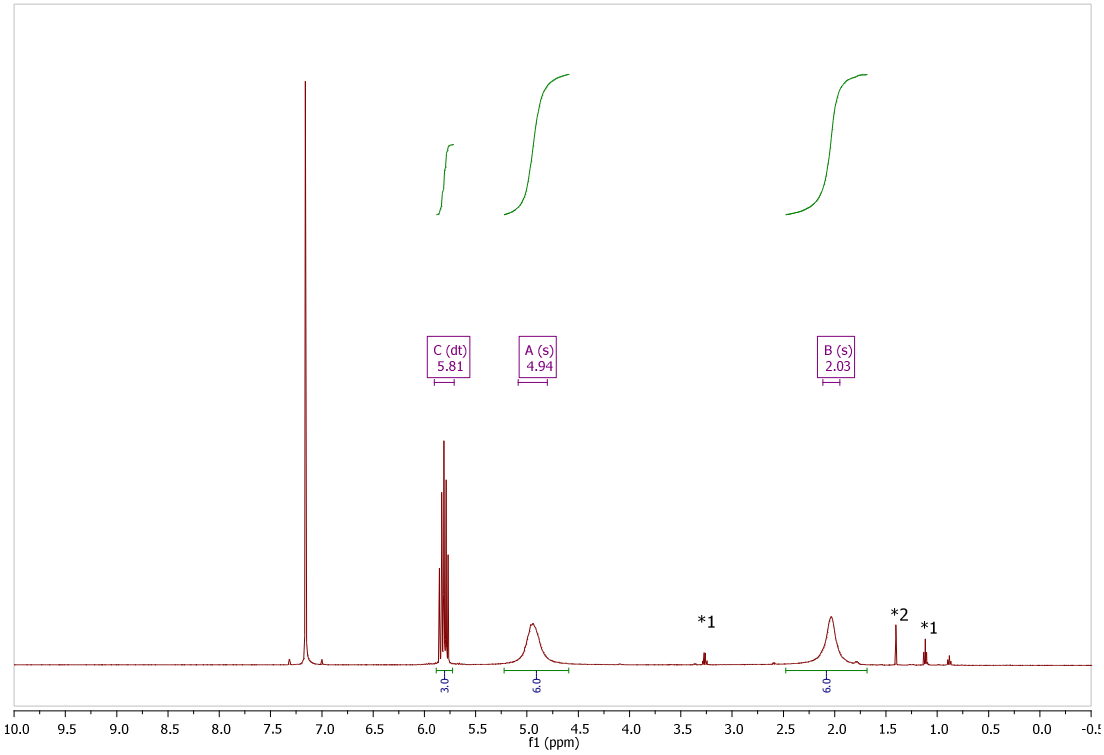


Figure SI- 1. ^{1}H NMR spectrum of triallylborane in C_6D_6.[c]

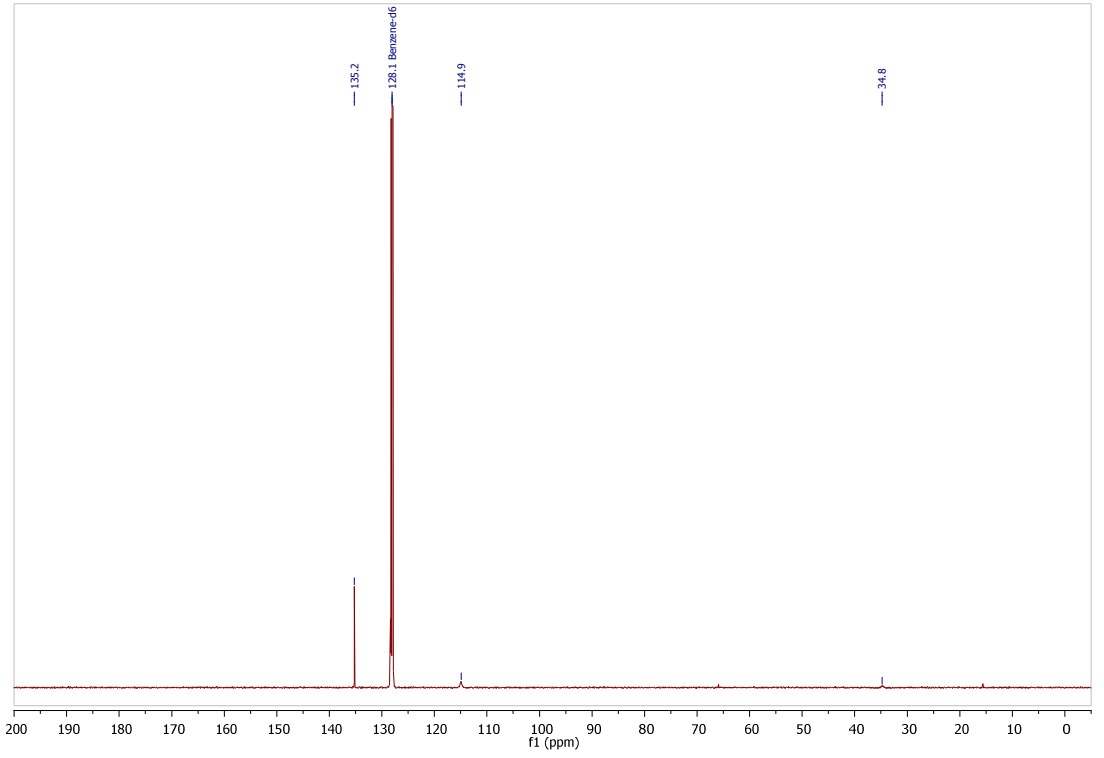


Figure SI- 2. $^{13}C\{^{1}H\}$ NMR spectrum of triallylborane in C_6D_6.

[c] The signals marked with *1 belong to the remaining solvent (diethyl ether) which could not be completely removed after three times fractionated distillation; the signal marked with *2 was attributed to cyclohexane which was an impurity of the NMR solvent batch.

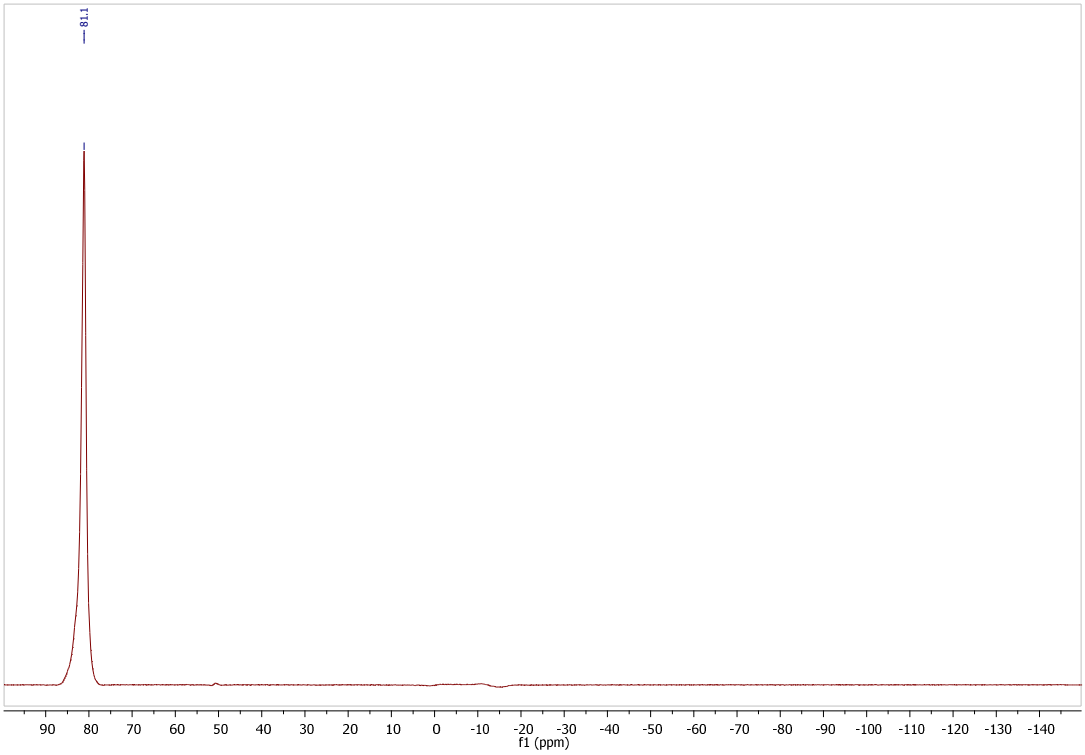
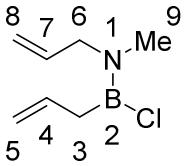
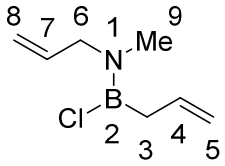


Figure SI- 3. ^{11}B NMR spectrum of triallylborane in C_6D_6.

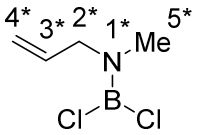
1,2-Diallyl-2-chloro-1-methylaminoborane[4]



a



b



by-product

Similar to the procedure of Lamm *et al.*:[2]

In a Schlenk flask a solution of BCl_3 (25.8 mL, 25.8 mmol, 1.00 M in hexanes) in *n*-pentane (180 mL) was cooled to -92 °C under an atmosphere of nitrogen. Triallylborane (1.73 g. 12.9 mmol) was added dropwise over a course of 1 min. The reaction mixture was stirred at -92 °C for 2 h before *N*-methylallylamine[3] (2.75 g, 38.6 mmol) and Et_3N (3.91 g, 38.6 mmol) in *n*-pentane (5 mL) were added dropwise using a syringe pump (0.12 mL/min). After addition, the mixture was allowed to warm to 22 °C. After 20 h of stirring, solvent was evaporated under inert conditions until approx. half volume and the mixture was filtrated through an syringe filter. Solvent evaporation (until 35 °C, 100 mbar) and subsequent Kugelrohr distillation (60 °C, 8 mbar) under inert conditions resulted in 1,2-Diallyl-2-chloro-1-methylaminoborane (2.721 g, 17.28 mmol, 45%) (1:1 mixture of **a** and **b**) which contained not separable by-product (7%). *Kugelrohr distillation led to a considerable amount of polymerized residue. Continuing with the crude mixture (~85-95 % calculated by ^{1}H NMR spectroscopy) resulted in a significantly higher yield after the next step (overall yield of more than 75 % after synthesis of 2-Chloro-1-methyl-3,6-dihydro-1,2-azaborine).*[d] ^{1}H NMR (500 MHz, C_6D_6) δ 5.99 (2 H, m, 4-$H_{a,b}$), 5.50 (1 H, m, 7-$H_{a/b}$), 5.33 (1 H, m, 7-$H_{a/b}$), 5.02 (4 H, m, 5-$H_{a/b}$), 4.89 (4 H, m, 8-$H_{a/b}$), 3.58 (2 H, m, 6-$H_{a/b}$), 3.22 (2 H, m, 6-$H_{a/b}$), 2.58 (3 H, s, 9-$H_{a/b}$), 2.29 (3 H, s, 9-$H_{a/b}$), 1.92 (4 H, m, 3-$H_{a/b}$); By-product: δ 3.36 (m, H-2*), 2.38 (s, H-5*); The other signals are covered by the product signals (confirmed by 2D NMR); ^{13}C{^{1}H} NMR (126 MHz, C_6D_6) δ 135.3, 135.1 (C-$4_{a,b}$), 134.8, 134.8 (C-$7_{a,b}$), 116.3, 116.1 (C-$8_{a,b}$), 115.0 (C-$5_{a,b}$), 54.5, 53.9 (C-$6_{a,b}$), 36.9, 36.1 (C-$9_{a,b}$);[e] By-product: δ 133.6 (C-3*), 116.9 (C-4*); The other signals are covered by the product signals (confirmed by 2D NMR); ^{11}B NMR (161 MHz, C_6D_6) δ 38.1; HRMS-EI$^+$ (*m/z*): $[M + H - (ClBAll)]^{+\bullet}$ calcd for C_4H_9N, 71.0735; found, 71.0736.

[d] With our available equipment IR spectroscopy cannot be performed for this air sensitive compound.
[e] The signal for the carbon (C-3) adjacent to boron was not visible in the ^{13}C NMR spectrum.

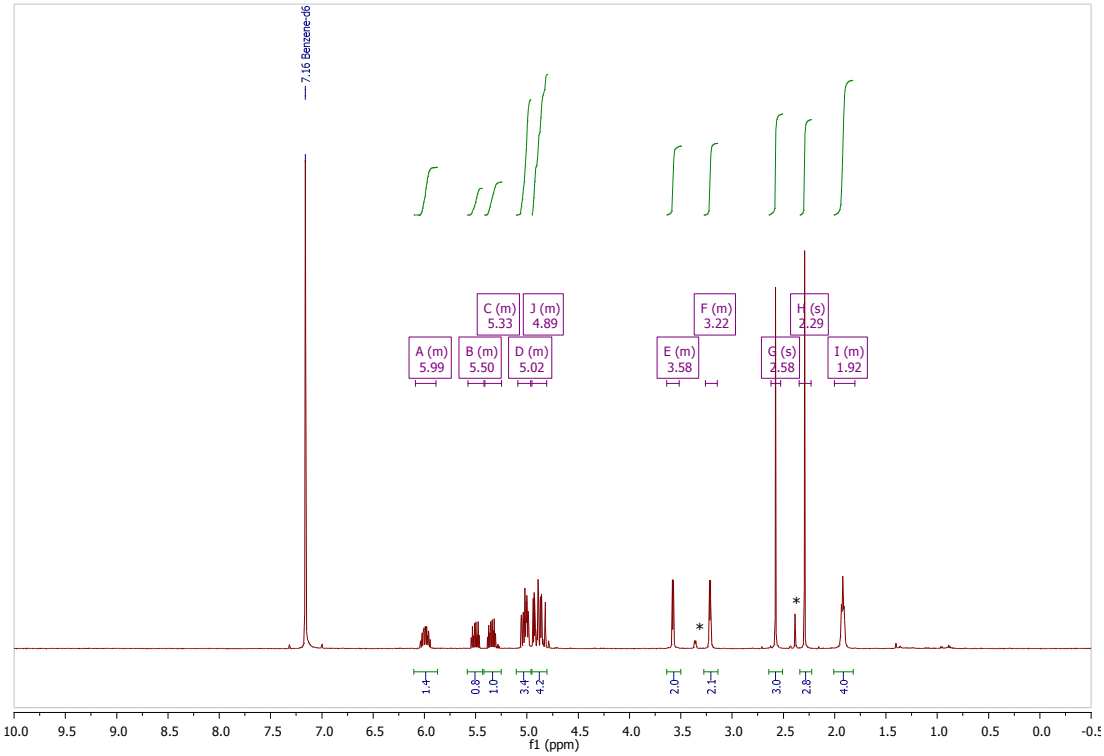


Figure SI- 4. ^{1}H NMR spectrum of 1,2-diallyl-2-chloro-1-methylaminoborane in C_6D_6..[f]

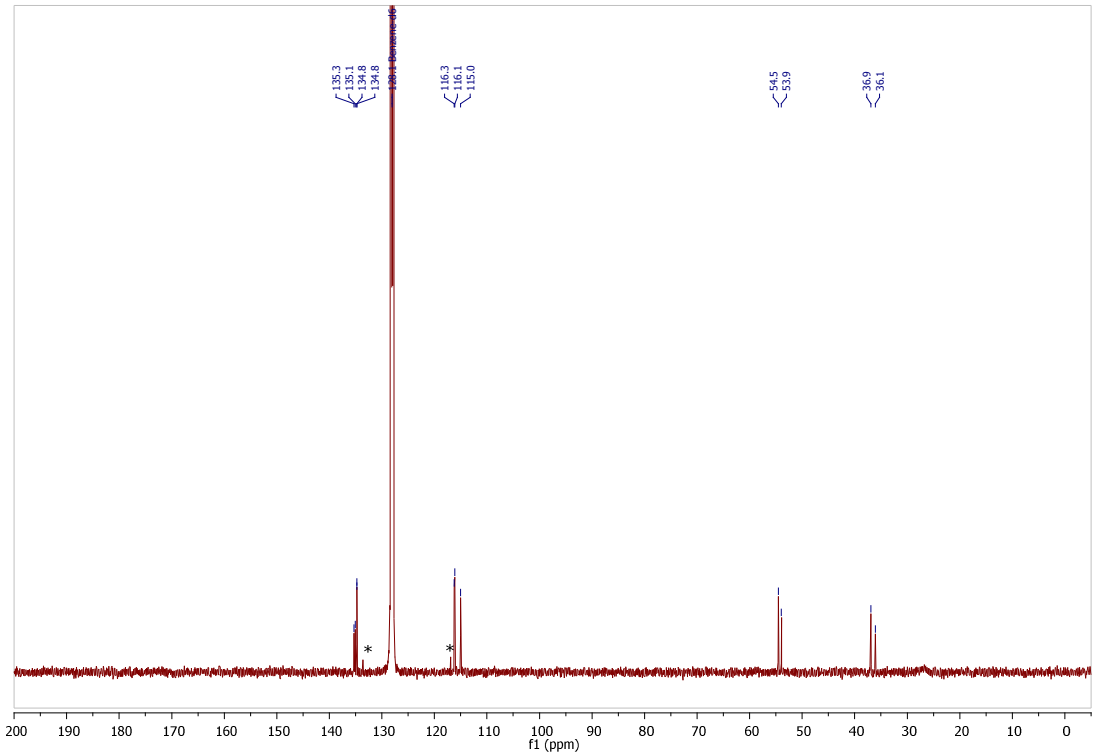


Figure SI- 5. ^{13}C{^{1}H} NMR spectrum of 1,2-diallyl-2-chloro-1-methylaminoborane in C_6D_6.**f**

[f] The signals marked with * are attributed to a by-product with two chlorides on boron which could not be separated.

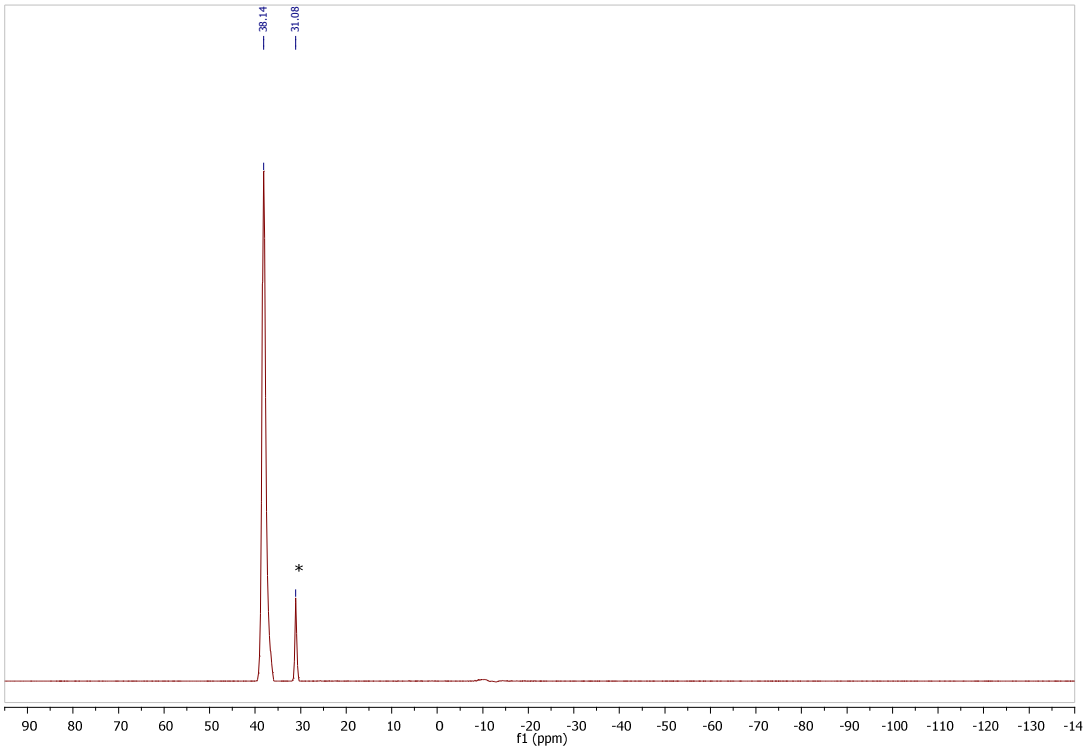
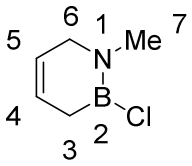


Figure SI- 6. ^{11}B NMR spectrum of 1,2-diallyl-2-chloro-1-methylaminoborane in C_6D_6.**f**

2-Chloro-1-methyl-3,6-dihydro-1,2-azaborine[4]



The procedure was adapted similar to Chrostowska et al.:[4]

In a glovebox, a 150 mL Schlenk flask was charged with Grubbs Cat. 1st Gen. (481 mg; 584 µmol; 1 mol%) and CH_2Cl_2 (110 mL). A solution of 1,2-diallyl-2-chloro-1-methylaminoborane (9.20 g; 58.4 mmol) in CH_2Cl_2 (24 mL) was added dropwise over the course of 2 min. to the catalyst solution. The mixture was stirred for 16 h at 21 °C before the solvent was removed under reduced pressure (40 °C, 200 mbar). Purification by Kugelrohr distillation under inert conditions (50 °C, 20 mbar) led to 2-Chloro-1-methyl-3,6-dihydro-1,2-azaborine (5.44 g, 42.0 mmol, 72%).[g] ^{1}H NMR (600 MHz, CD_2Cl_2) δ 5.72 (1 H, bs, 4-H), 5.58 (1 H, m, 5-H), 3.64 (2 H, m, 6-H), 2.89 (3 H, s, 7-$H_{a/b}$), 1.66 (2 H, bs, 3-H); ^{13}C{^{1}H} NMR (151 MHz, CD_2Cl_2) δ 125.4 (C-4), 124.5 (C-5), 52.6 (C-6), 38.1 (C-3), 18.8 (C-7). ^{11}B NMR (161 MHz, CD_2Cl_2) δ 37.5; HRMS-EI$^+$ (*m/z*): [M-O-M]$^{+\bullet}$ calcd for $C_{10}H_{17}B_2N_2O$, 203.1527; found, 203.1524.[h]

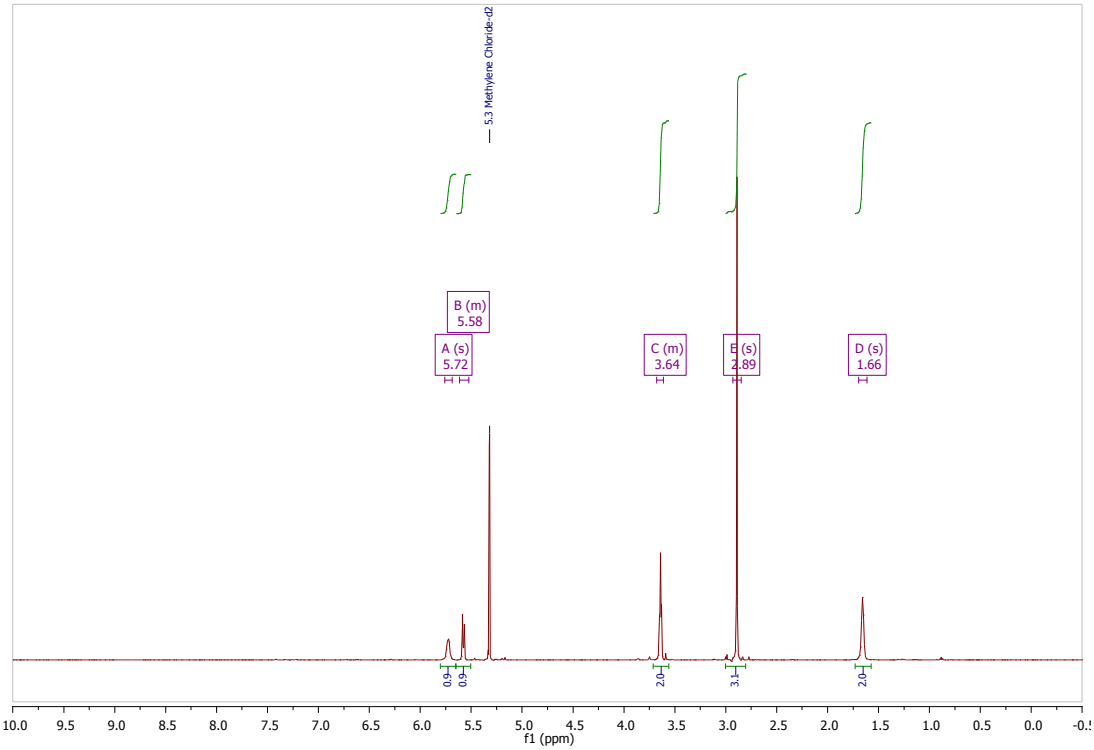


Figure SI- 7. ^{1}H NMR spectrum of 2-chloro-1-methyl-3,6-dihydro-1,2-azaborine in CD_2Cl_2.

[g] With our available equipment, high resolution mass spectrometry and IR spectroscopy cannot be performed for air sensitive compounds.
[h] Obviously, the compound formed the corresponding anhydride species due to hydrolysation.

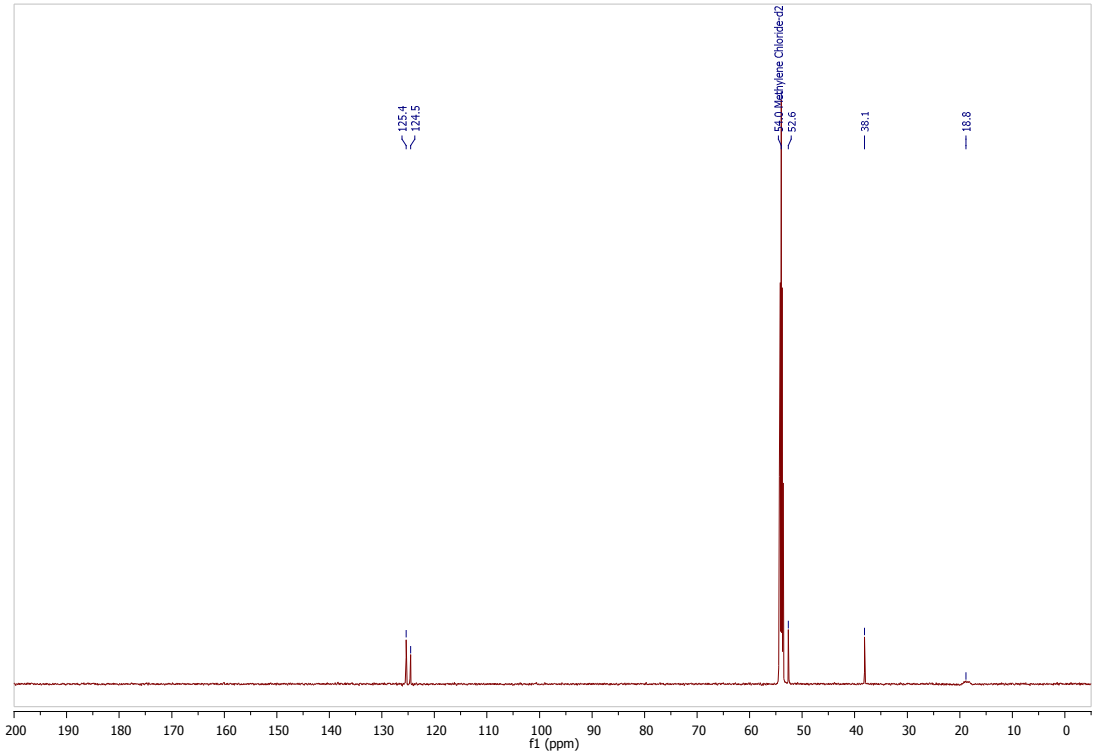


Figure SI- 8. $^{13}C\{^{1}H\}$ NMR spectrum of 2-chloro-1-methyl-3,6-dihydro-1,2-azaborine in CD_2Cl_2..

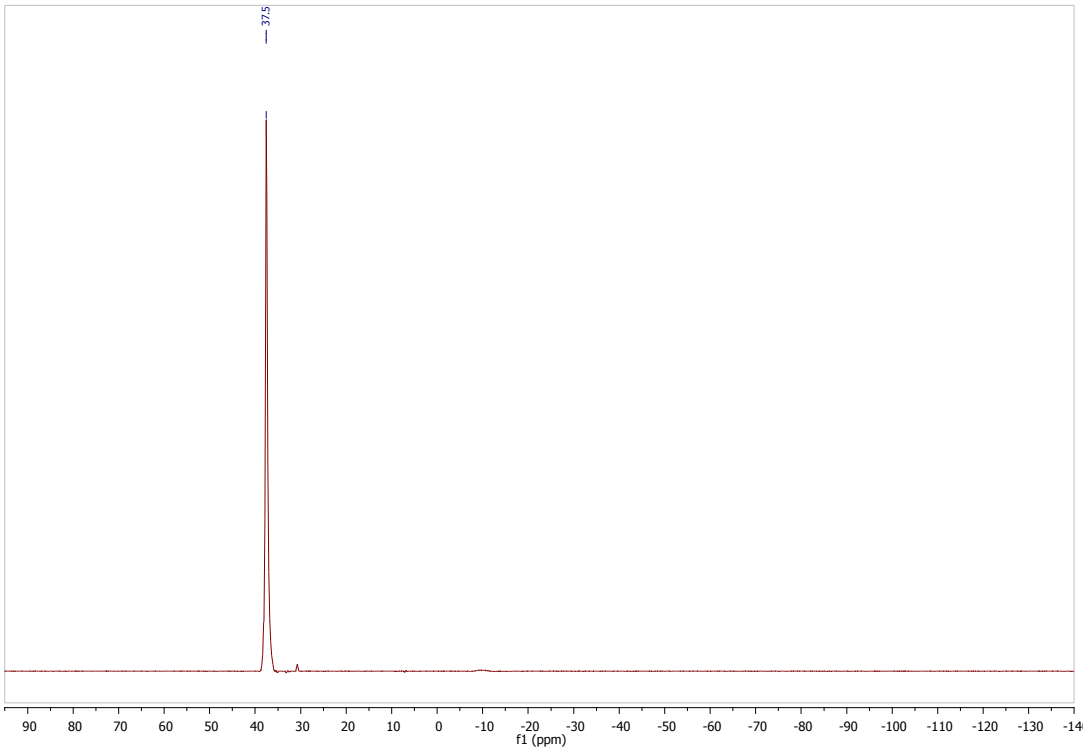
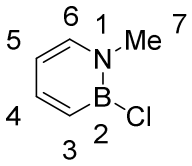


Figure SI- 9. ^{11}B NMR spectrum of 2-chloro-1-methyl-3,6-dihydro-1,2-azaborine in CD_2Cl_2..

2-Chloro-1-methyl-1,2-azaborine (1)[4]



The procedure was adapted similar to Chrostowska et al.:[4]

In a glovebox, a dry microwave vial was charged with Pd black (164 mg; 1.55 mmol), cyclohexene (20 mL) and 2-chloro-1-methyl-3,6-dihydro-1,2-azaborine (1.50 g; 11.6 mmol) was added. The flask was sealed with a microwave cap. The mixture was stirred and heated for 6 h at 120 °C in the microwave. Subsequently, the reaction mixture was filtered through a PTFE syringe filter (pore size = 0.45 µm), the solvent was removed under reduced pressure and Kugelrohr distillation under inert conditions (65 °C, 20 mbar) resulted in azaborine 1 (985 mg, 7.73 mmol, 67%).[i] ^{1}H NMR (500 MHz, CD_2Cl_2) δ 7.56 (1 H, bs, 4-H), 7.22 (1 H, m, 6-H), 6.62 (1 H, m, 3-H), 6.30 (1 H, m, 5-H), 3.59 (3 H, s, 7-H); ^{13}C{^{1}H} NMR (126 MHz, CD_2Cl_2) δ 145.2 (C-4), 140.6 (C-6), 127.7 (C-3), 111.0 (C-5), 41.3 (C-7);[j] ^{11}B NMR (161 MHz, CD_2Cl_2) δ 32.8; HRMS-EI^{+} (*m/z*): $[M\text{-}O\text{-}M]^{+\bullet}$ calcd for $C_{10}H_{13}B_2N_2O$, 199.1214; found, 199.1207.[k]

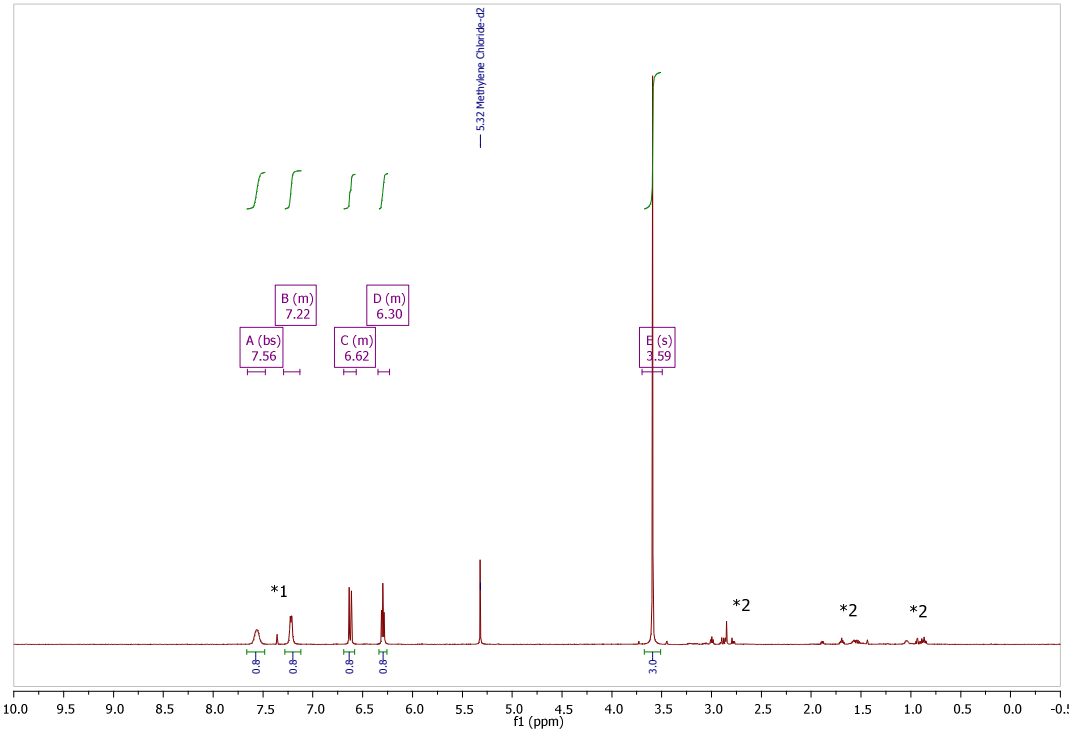


Figure SI- 10. ^{1}H NMR spectrum of 2-chloro-1-methyl-1,2-azaborine (**1**) in CD_2Cl_2; *1 = traces benzene (by-product); *2 = not separable traces of undefined by-products.

[i] With our available equipment, IR spectroscopy cannot be performed for this air sensitive compound.
[j] The signal intensity for the carbon atom next to the boron atom (C-3) in the ^{13}C NMR spectrum was very low.
[k] Obviously, the compound formed the corresponding anhydride species due to hydrolysation.

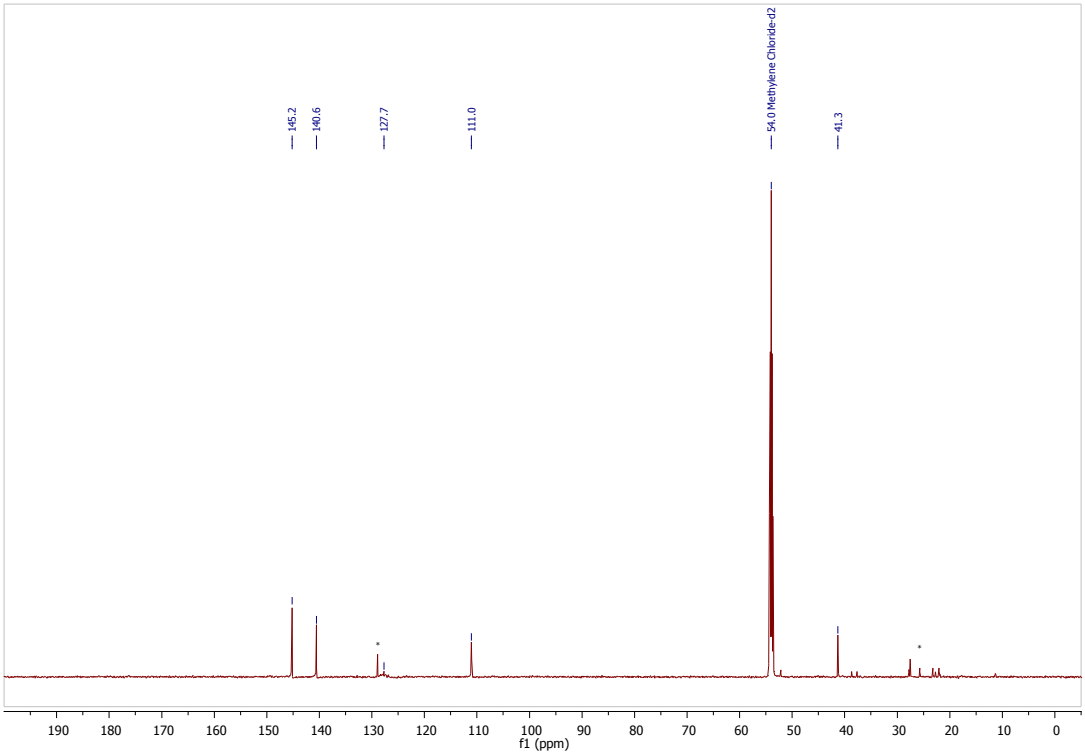


Figure SI- 11. $^{13}C\{^{1}H\}$ NMR spectrum of 2-chloro-1-methyl-1,2-azaborine (**1**) in CD_2Cl_2.[l]

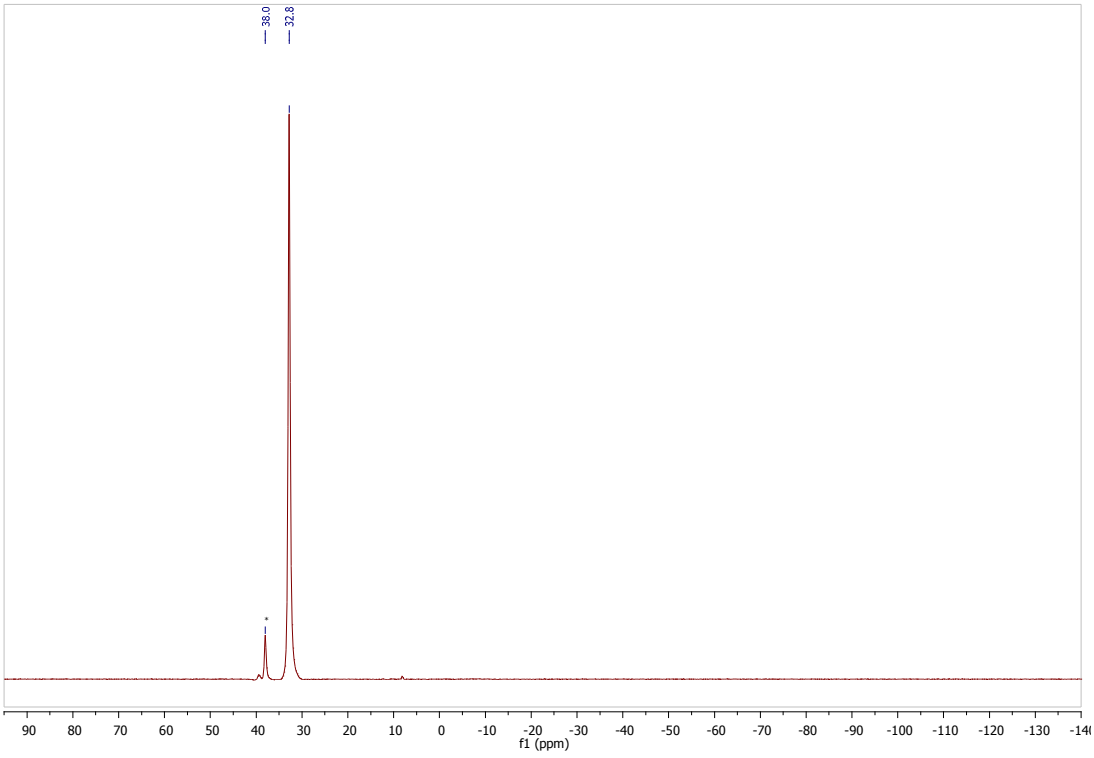
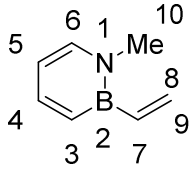


Figure SI- 12. ^{11}B NMR spectrum of 2-chloro-1-methyl-1,2-azaborine (**1**) in CD_2Cl_2.[m]

[l] The signals marked with * were attributed to benzene and cyclohexane (+ undefined) residues from the reaction which was not absolutely separable after several Kugelrohr distillations.
[m] The signals market with *were attributed to the to hydrolyzed by-product, which was not separable,.

1-Methyl-2-vinyl-1,2-azaborine (2)



Preparation of vinyl lithium (according to Seyferth et al.)[5]:

In a Schlenk tube under an N_2 atmosphere, *n*-butyllithium (8.0 mL, 20 mmol; 2.5 M in hexanes) was added dropwise to tetravinyl stannane (2.39 g, 10.00 mmol) over the course of 3 min. A precipitate was formed. After letting it settle, the solvent was removed via syringe and the solid was washed 4 times with *n*-pentane (4 mL). Finally, vinyllithium was dissolved in diethylether (10 mL). Concentration (0.59 M; 59 % yield) was determined by titration (menthol/2,2-bipyridyl).[6]

Vinylation procedure adapted according to the procedure of Marwitz et al. for another compound:[7]

Under a N_2 atmosphere, a 100 mL Schlenk flask was filled with **1** (1.15 g, 9.00 mmol) and degassed Et_2O (80 mL). The solution was cooled down to -92 °C (N_2/acetone bath) before vinyllithium (10.8 mL, 10.8 mmol, 1 M in Et_2O) was added dropwise using a syringe pump (0.5 mL/min). After addition, the solution was stirred for further 2 h at -92 °C before it was allowed to warm up to 22 °C by removing the cooling bath. The mixture was concentrated to ca. 30 mL before it was filtered through a syringe filter. Removing of solvent (40 °C, 150 mbar) and Kugelrohr distillation (65 °C, 20 mbar) gave azaborine **2** (765 mg, 6.43 mmol, 71%). ^{1}H NMR (500 MHz, CD_2Cl_2) δ 7.53 (1 H, dd, *J* = 11.0, 6.6 Hz, 4-H), 7.15 (1 H, d, *J* = 6.6 Hz, 6-H), 6.89 (1 H, dd, *J* = 11.0, 1.5 Hz, 3-H), 6.63 (1 H, dd, *J* = 19.5, 13.6 Hz, 7-H), 6.25 (1 H, ddd, *J* = 6.6, 6.6, 1.5 Hz, 5-H), 6.06 (1 H, dd, *J* = 19.5, 3.9 Hz, 8-H), 5.92 (1 H, dd, *J* = 13.6, 3.9 Hz, 9-H), 3.59 (1 H, s, 10-H); ^{13}C{^{1}H} NMR (126 MHz, CD_2Cl_2) δ 143.0 (C-4), 140.3 (C-6), 137.9 (C-7), 130.9 (C-8,9), 128.0 (C-3), 111.1 (C-5), 42.0 (C-10); ^{11}B NMR (161 MHz, CD_2Cl_2) δ 33.4; HRMS[n].

[n] With our available equipment, high resolution mass spectrometry and IR spectroscopy cannot be performed for this air sensitive compound.

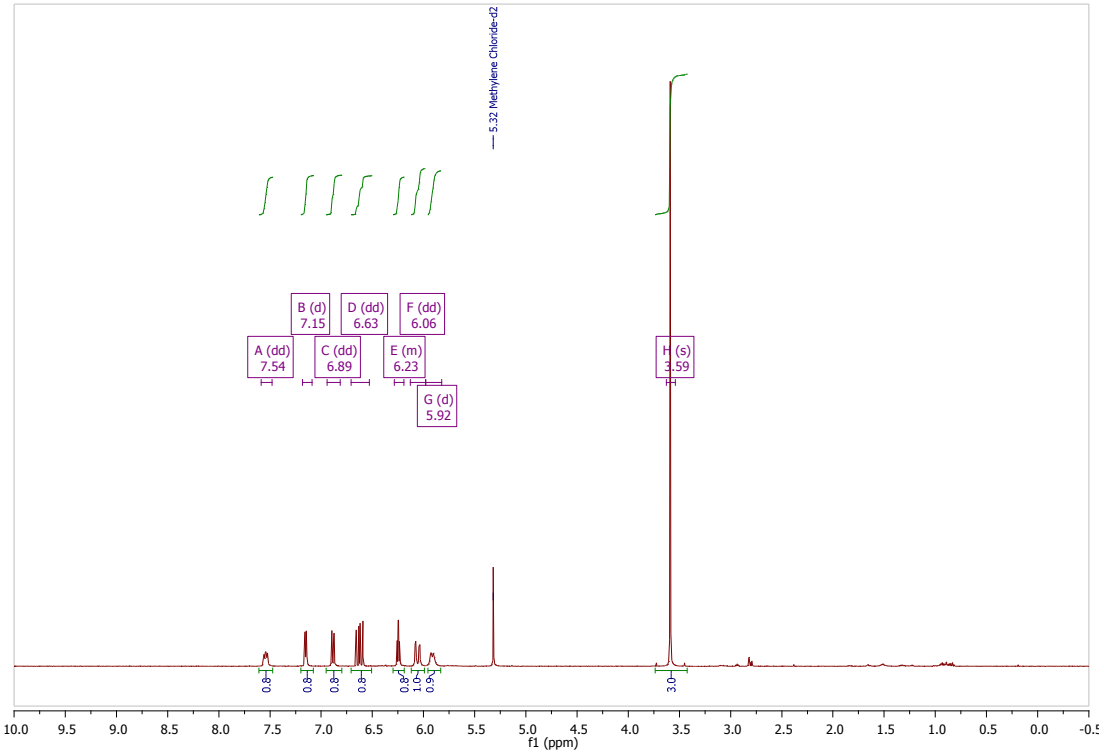


Figure SI- 13. ^{1}H NMR spectrum of 1-methyl-2-vinyl-1,2-azaborine (**2**) in CD_2Cl_2.

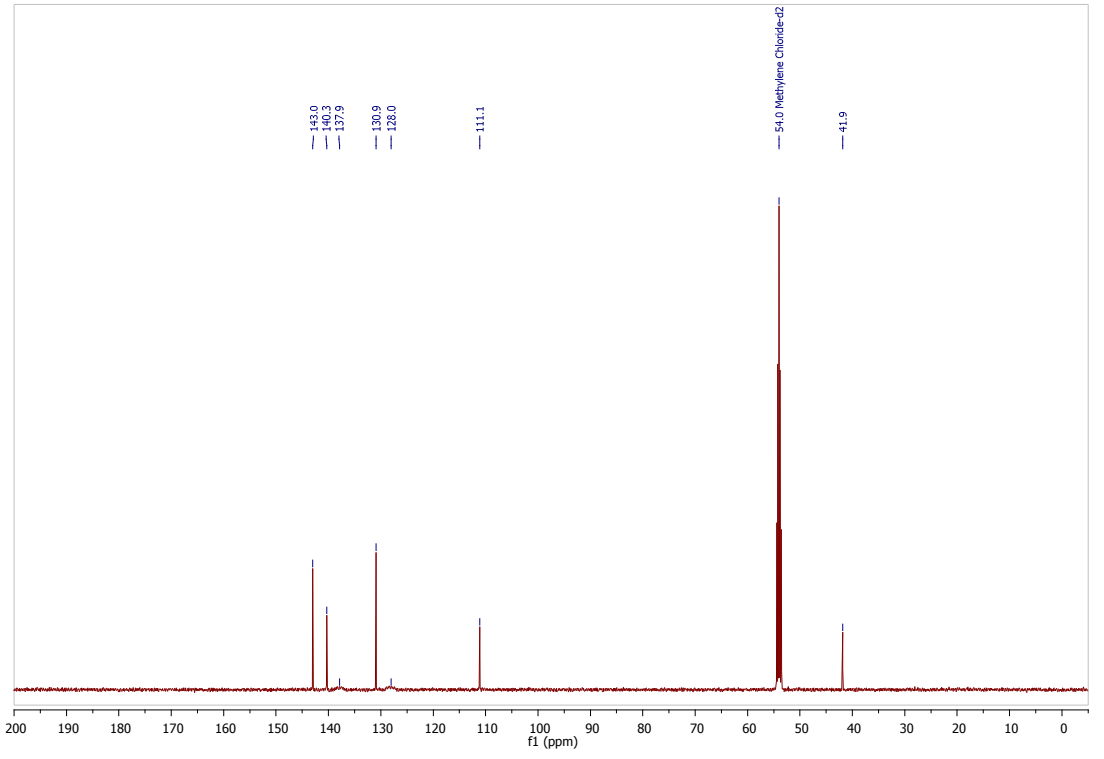


Figure SI- 14. ^{13}C{^{1}H} NMR spectrum of 1-methyl-2-vinyl-1,2-azaborine (**2**) in CD_2Cl_2.

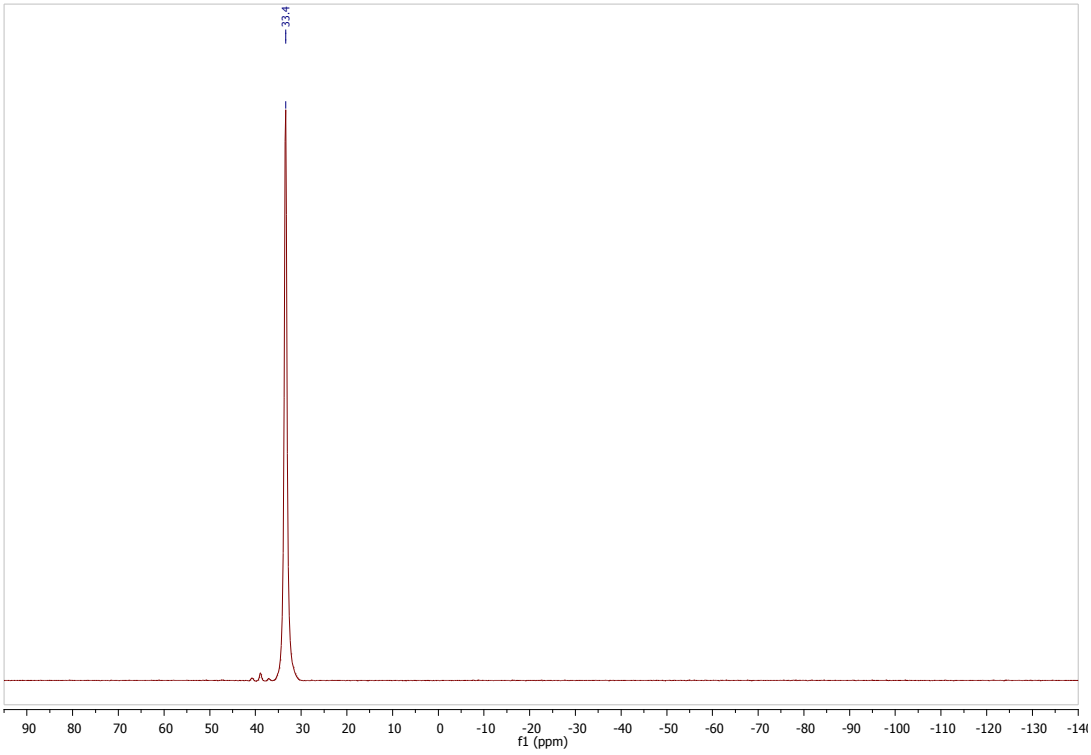
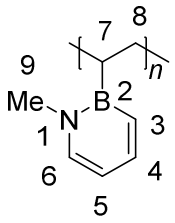


Figure SI- 15. ^{11}B NMR spectrum of 1-methyl-2-vinyl-1,2-azaborine (**2**) in CD_2Cl_2.

Polymerizations and Characterizations

Poly(1-methyl-2-vinylazaborine) (3)



Under a nitrogen atmosphere, 1-methyl-2-vinylazaborine (303 mg, 2.55 mmol) and AIBN (4 mg, 25 µmol, 1 mol%) were placed into a dried J Young's tube. The mixture was transferred into a preheated oil bath (85 °C) and heated for 72 h until the mixture became highly viscous. The polymer was then dissolved in toluene (2 mL) and precipitated into methanol (6 mL). The polymer was dried under reduced pressure ($4x10^{-2}$ mbar, 40 °C oil bath) to yield in poly(1-methyl-2-vinylazaborine) (**3**) (153 mg, 51%). [For redissolving and transferring into a storage bottle dichloromethane was used due to low solubility in toluene]. ^{1}H NMR (600 MHz, C_6D_6) δ 7.52 (1 H, bm, 4-H), 6.98 (1 H, bm, 6-H), 6.64 (1 H, bm, 3-H), 6.15 (1 H, bm, 5-H), 2.92 (3 H, bm, 9-H), 1.50 (3 H, bm, 7-H,8-H); ^{13}C{^{1}H} NMR (151 MHz, C_6D_6) δ 141.4 (C-4), 139.2 (C-6), 129.9 (C-3), 109.4 (C-5), 40.8 (C-9), 39.8 (C-7), 28.0 (C-8); ^{11}B NMR (161 MHz, C_6D_6) δ 44; ^{1}H NMR (600 MHz, CD_2Cl_2) δ 7.21 (1 H, bm, 4-H), 6.89 (1 H, bm, 6-H), 6.43 (1 H, bm, 3-H), 6.02 (1 H, bm, 5-H), 3.20 (3 H, bm, 9-H), 1.14 (3 H, bm, 7-H,8-H); ^{13}C{^{1}H} NMR (151 MHz, CD_2Cl_2) δ 141.5 (C-4), 139.6 (C-6), 129.5 (C-3), 109.5 (C-5), 41.1 (C-9), 39.3 (C-7), 27.7 (C-8); IR (ATR) ν_{max}/cm^{-1} 3067, 3000, 2895, 2836, 1612, 1514, 1463, 1416, 1397, 1311, 1225, 732, 697; MS[o]; M_W = 24900 g/mol (eluent: THF, elution at 1 mL/min, 35 °C, universal calibration); PDI = 1.51.

[o] The polymer could not be analysed by mass spectrometry (MALDI, ESI).

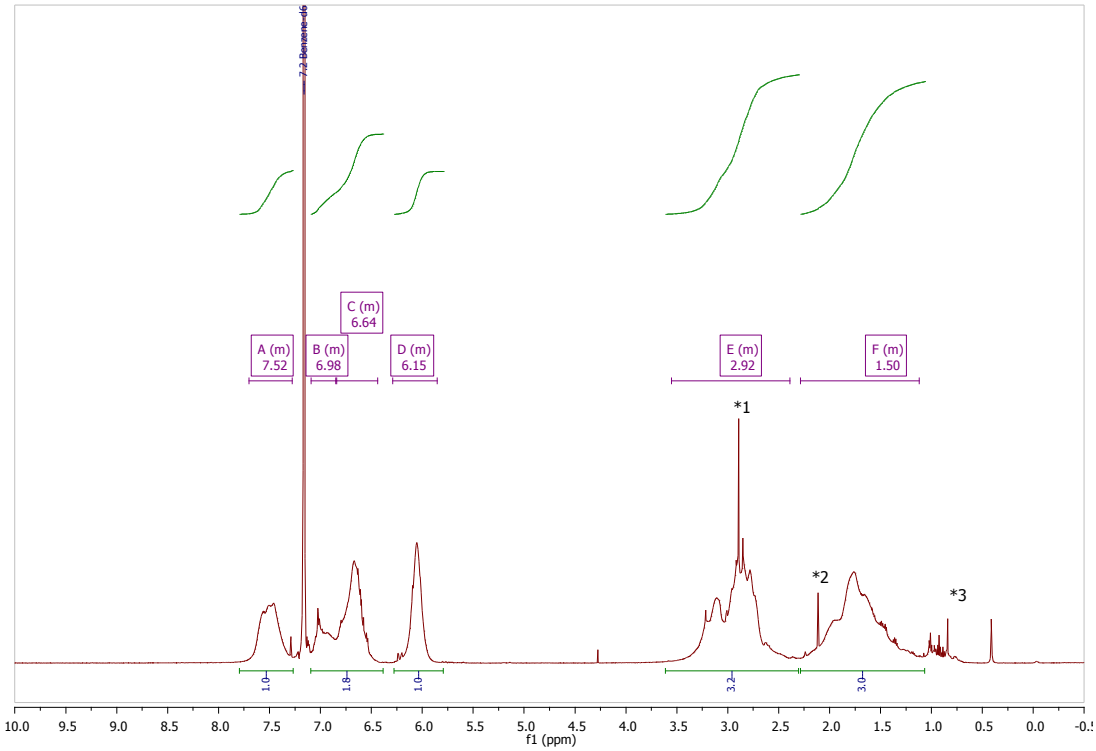


Figure SI- 16. ^{1}H NMR spectrum of poly(1-methyl-2-vinylazaborine) (**3**) in C_6D_6; *1 = starting material; *2 = toluene; *3 = undefined signals.

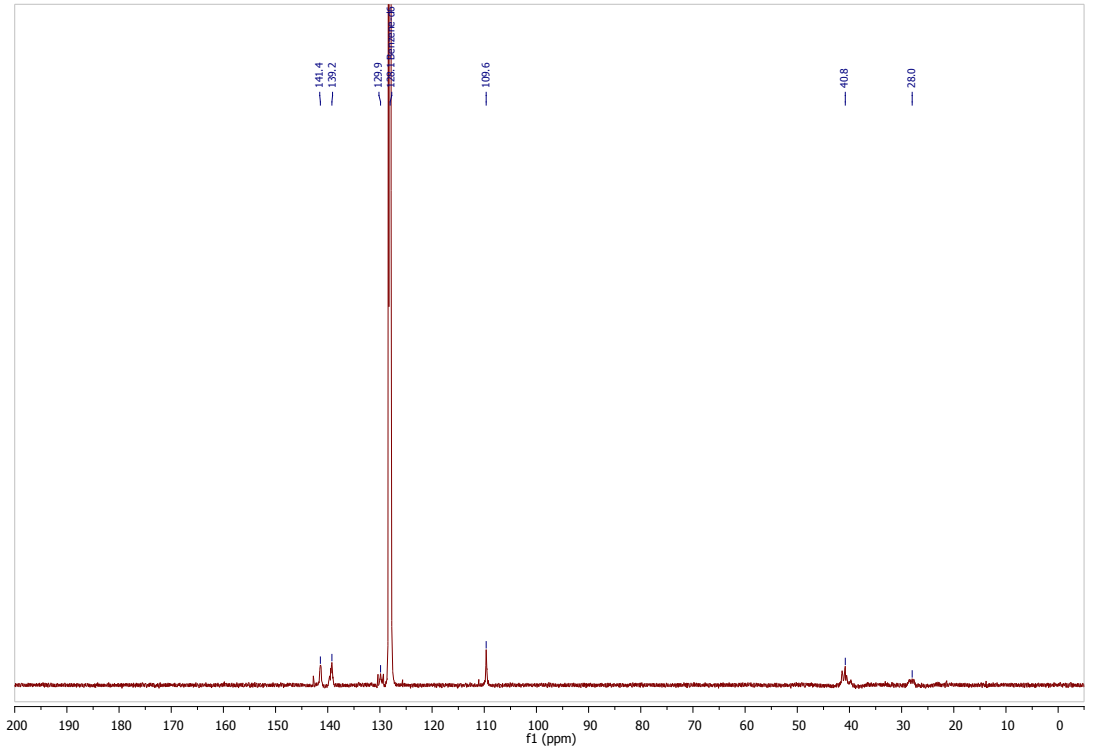


Figure SI- 17. ^{13}C{^{1}H} NMR spectrum of poly(1-methyl-2-vinylazaborine) (**3**) in C_6D_6.

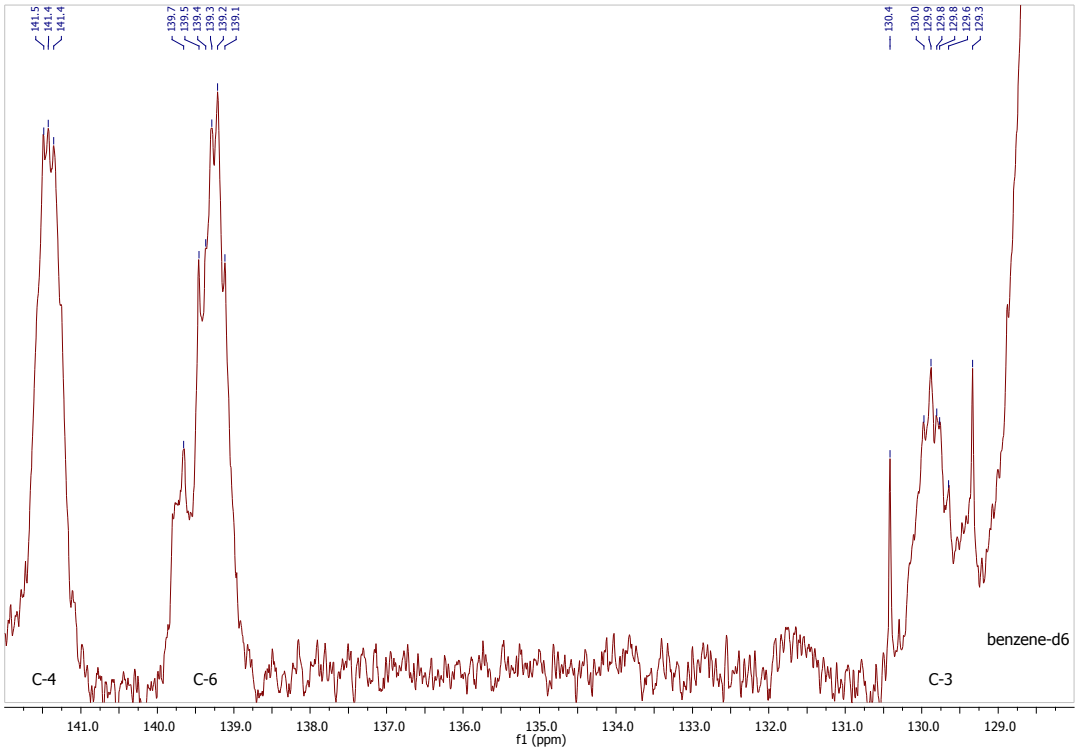


Figure SI- 18. Section of the $^{13}C\{^{1}H\}$ NMR spectrum of poly(1-methyl-2-vinylazaborine) (**3**) in C_6D_6.

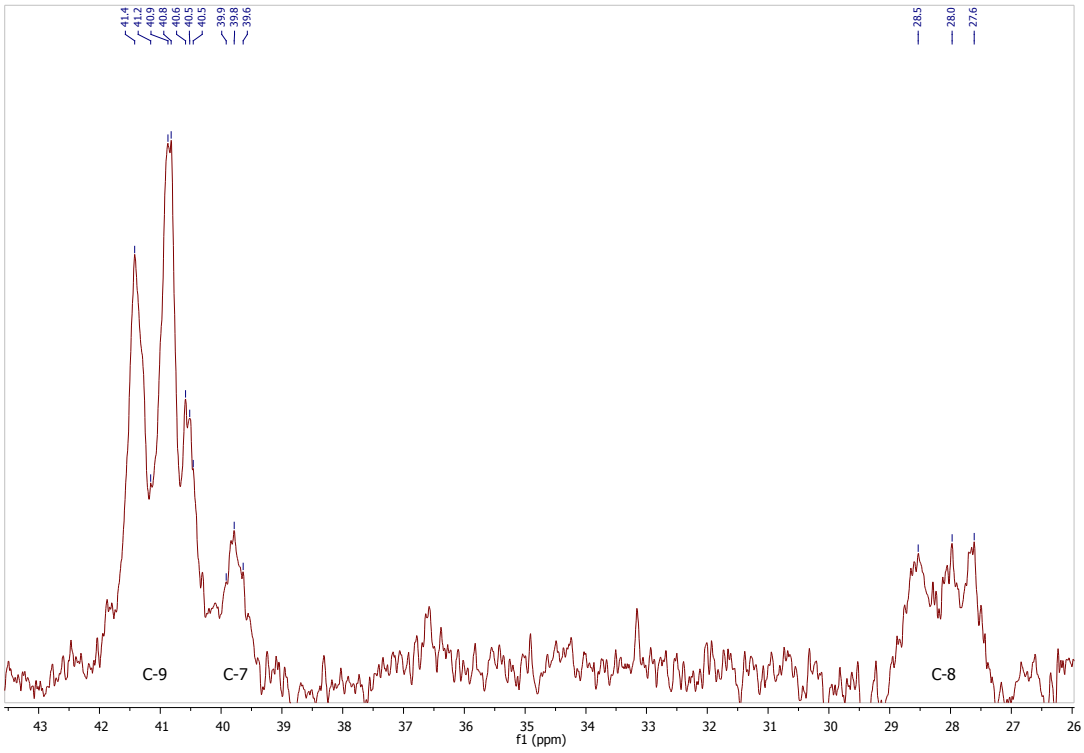


Figure SI- 19. Section of the $^{13}C\{^{1}H\}$ NMR spectrum of poly(1-methyl-2-vinylazaborine) (**3**) in C_6D_6.

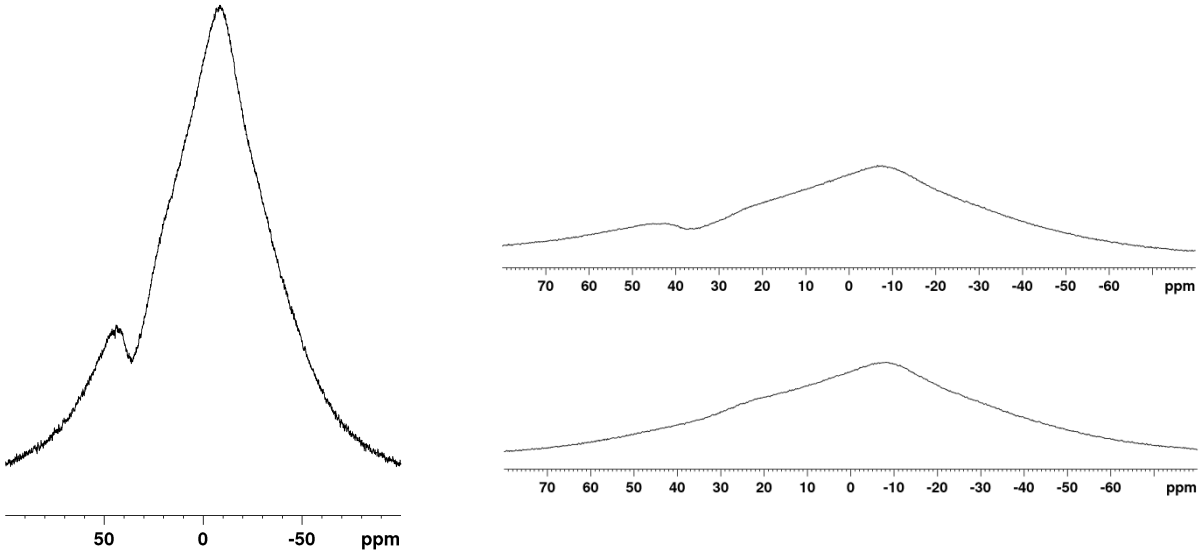


Figure SI- 20. Left: ^{11}B NMR spectrum of poly(1-methyl-2-vinylazaborine) (**3**) in C_6D_6; Right top: ^{11}B NMR spectrum of poly(1-methyl-2-vinylazaborine) (**3**) in C_6D_6 in a quartz NMR tube compared to an ^{11}B NMR spectrum of pure C_6D_6 solvent (bottom) for comparison. The broad signal centred at ca. -8 ppm originates from boron-containing materials in the probe head, with the broad boron-signal arising from compound **3** at ~44 ppm.

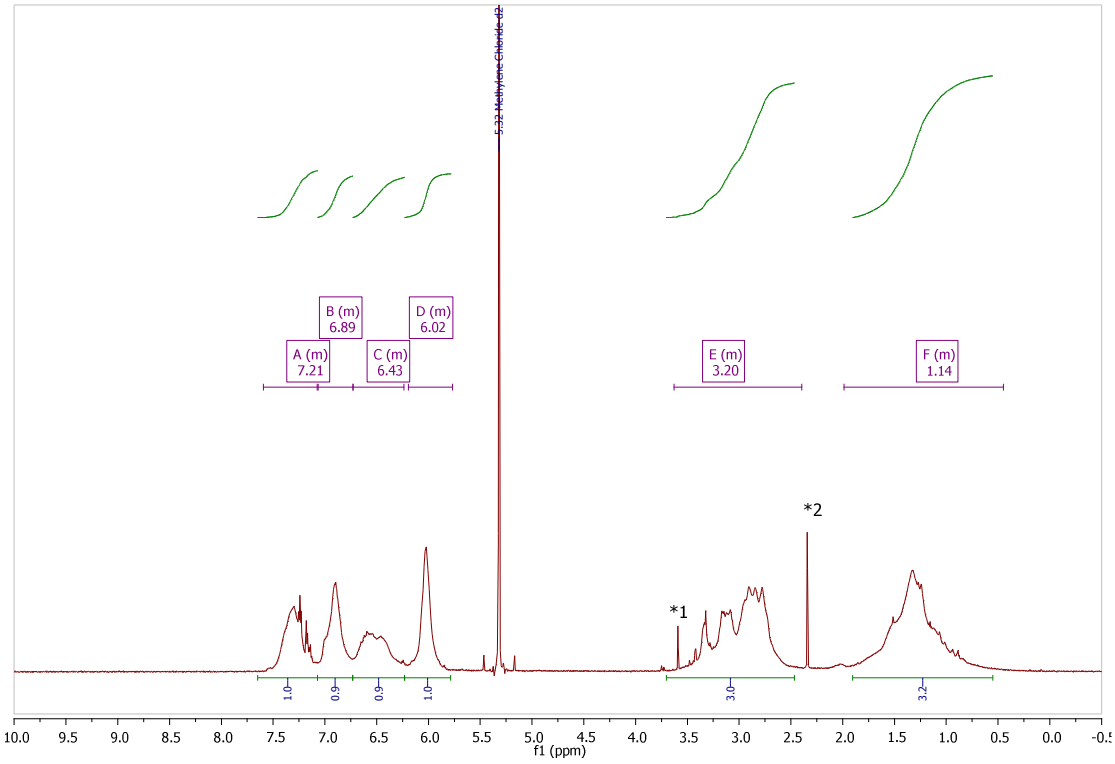


Figure SI- 21. ^{1}H NMR spectrum of poly(1-methyl-2-vinylazaborine) (**3**) in CD_2Cl_2; *1 = starting material; *2 = toluene.

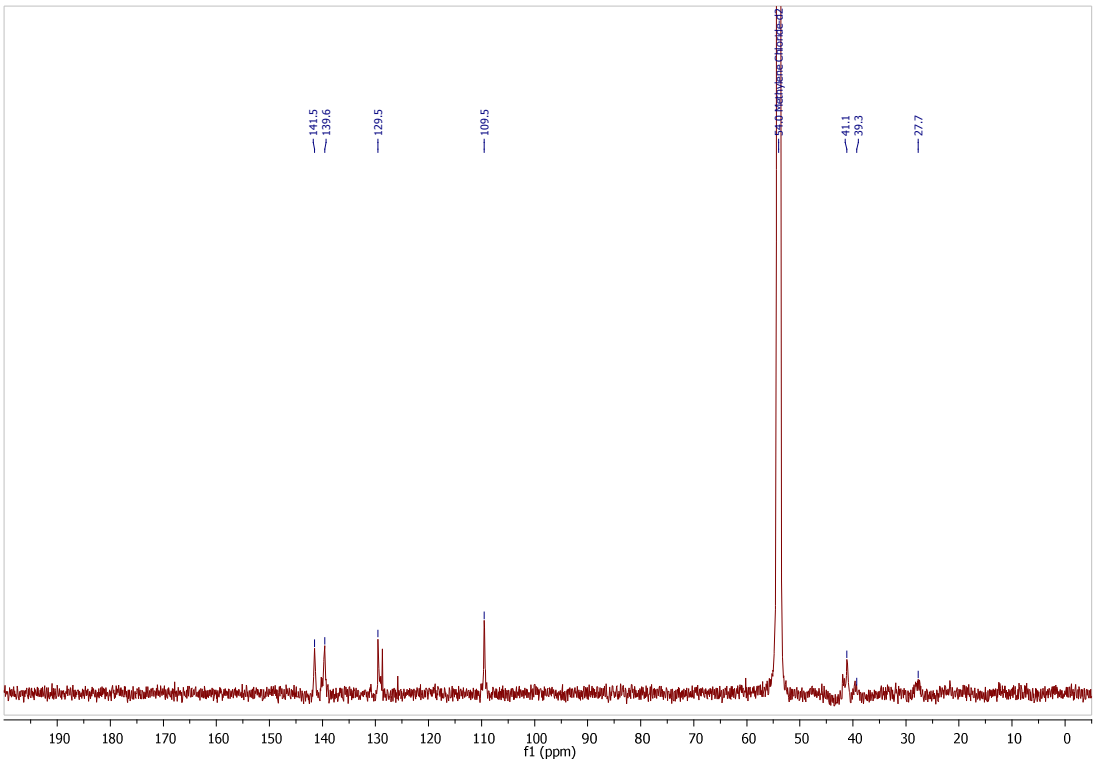


Figure SI- 22. $^{13}C\{^{1}H\}$ NMR spectrum of poly(1-methyl-2-vinylazaborine) (**3**) in CD_2Cl_2.

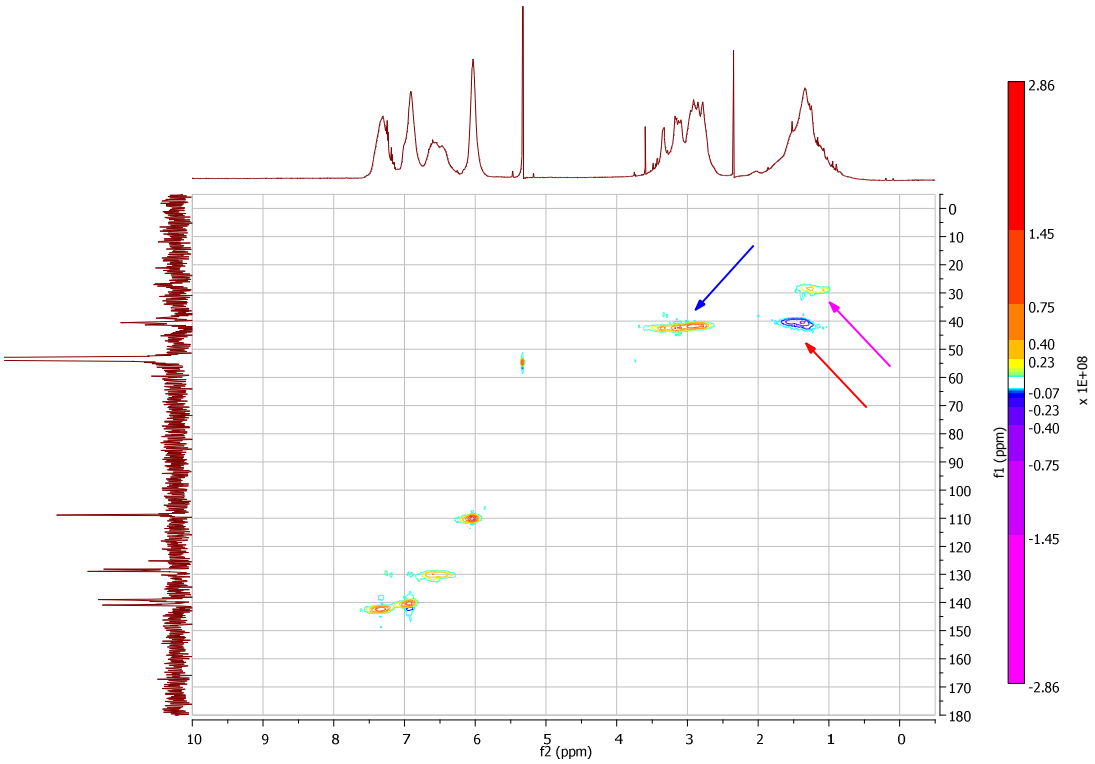


Figure SI- 23. HSQC-DEPT experiment in CD_2Cl_2 for assigning the ^{1}H and ^{13}C signals of **3**. The signal for the *N*-methyl groups are clearly visible (blue arrow); In the signal for the olefinic backbone, there is a signal for a methylene group (red arrow) and a further signal for the CH-group (purple arrow). There is no evidence that the *N*-methyl group has reacted during the radical polymerization.

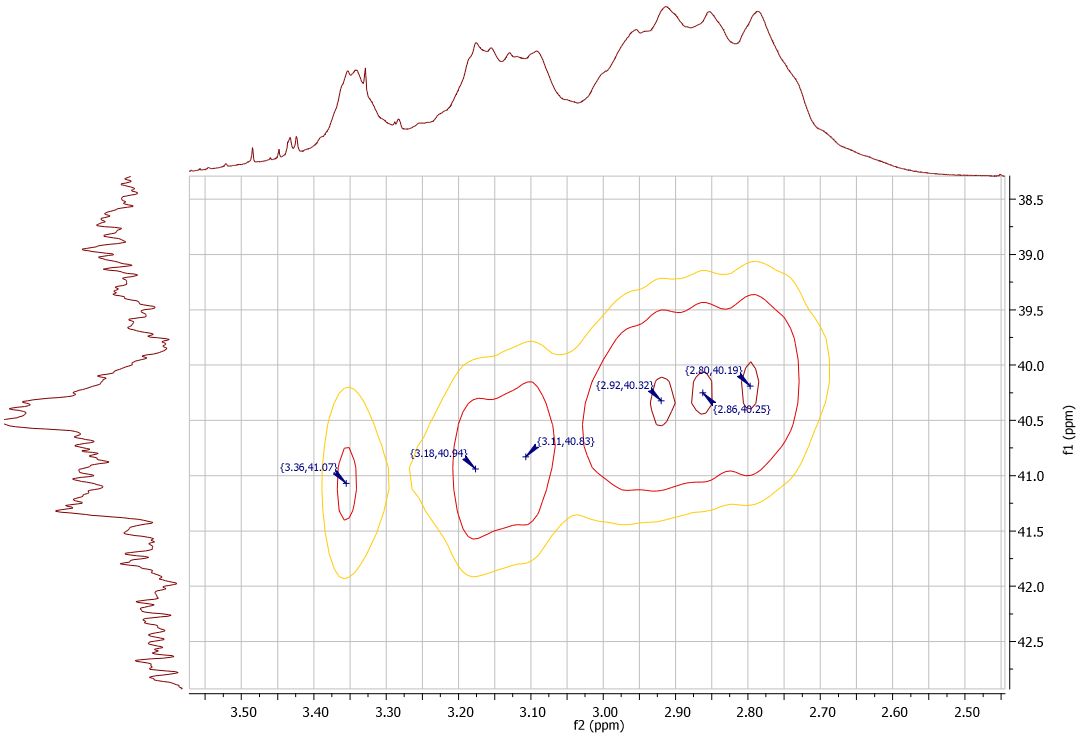


Figure SI- 24. Section of the HSQC NMR spectrum of poly(1-methyl-2-vinylazaborine) (**3**) in CD_2Cl_2.

Table SI- 2. GPC results of poly(1-methyl-2-vinylazaborine) (**3**) measured in THF; Conventional calibration was performed with polystyrene standards (narrow distribution) and a refractive index detector; Universal calibration was performed with additional on-line viscometer detection.

	Conventional Calibration	**Universal Calibration**
Mn (g/mol)	6470	16500
Mw (g/mol)	10300	24900
PDI	1.59	1.51

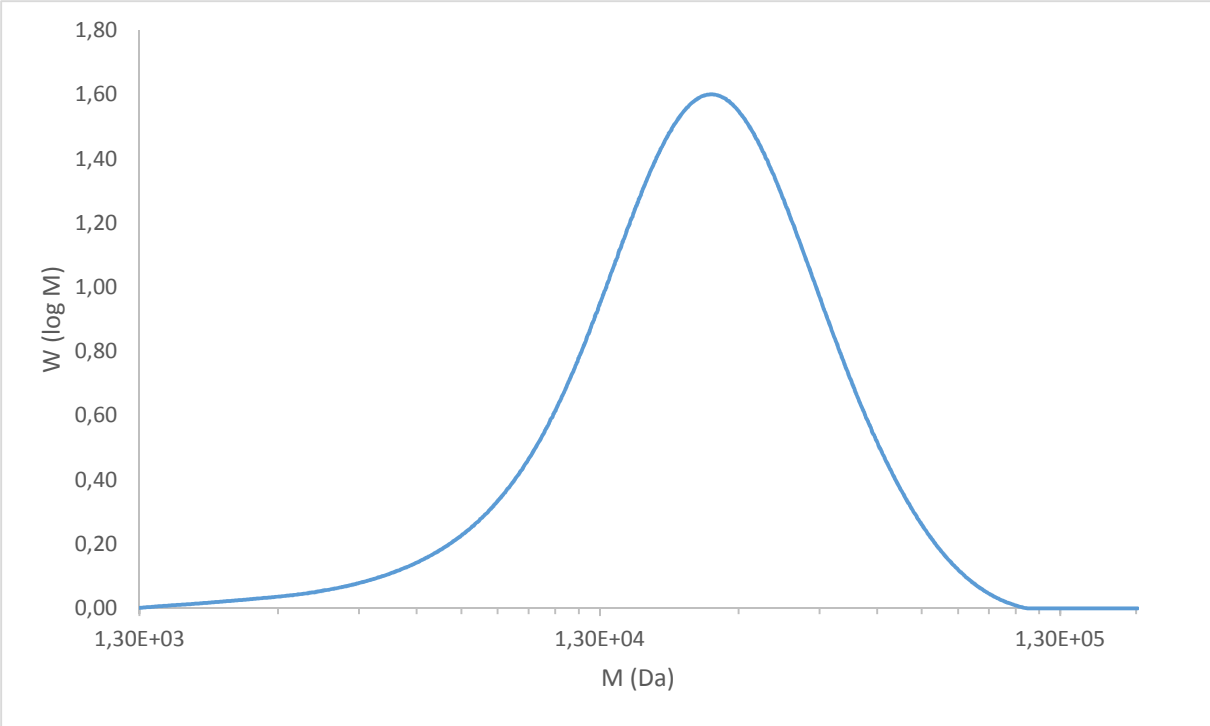


Figure SI- 25. Mass distribution diagram of poly(1-methyl-2-vinylazaborine) (**3**) measured in THF.

DSC

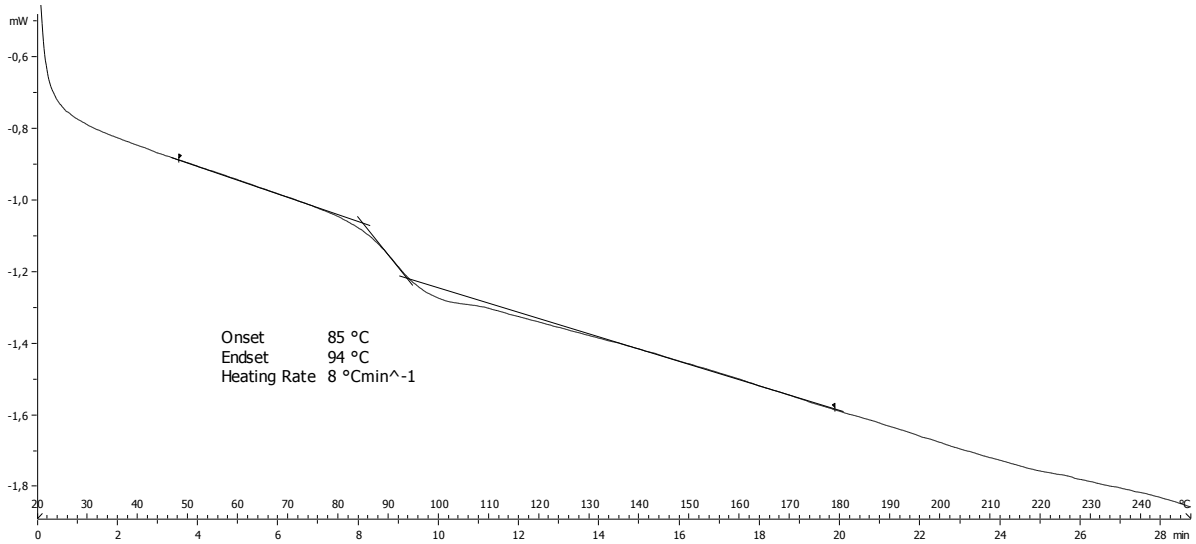


Figure SI- 26. Differential scanning calorimetry of poly(*N*-methyl-2-vinylazaborine) (**3**) under a nitrogen atmosphere; sample weight: 4.4292 mg; heating rate: 8.00 K/min; crucible: 40 µL aluminium; Tg: 85 °C (onset); exo up.

TGA

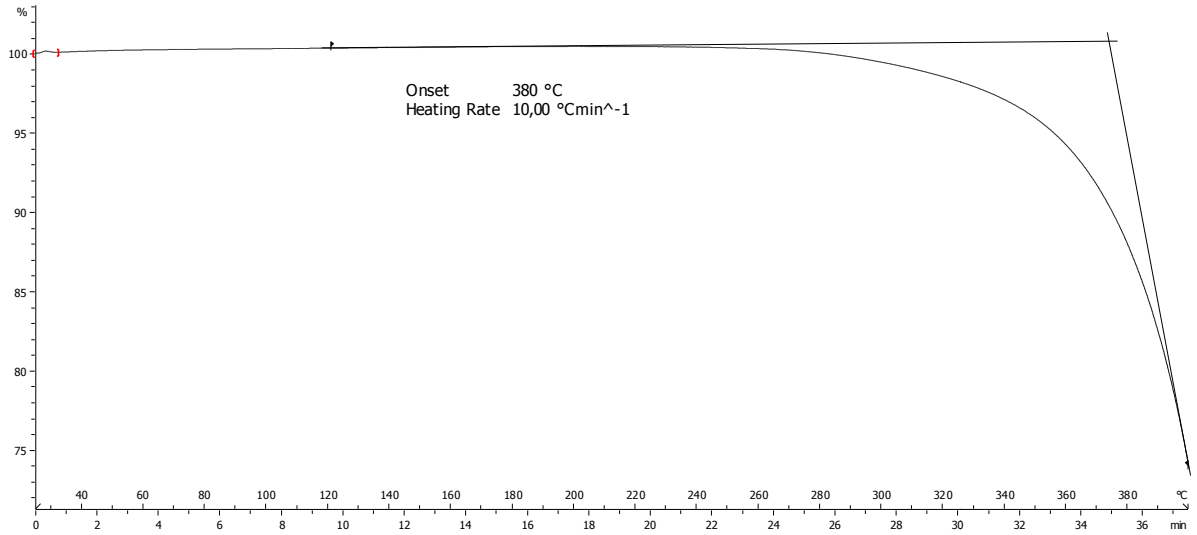


Figure SI- 27. Thermogravimetric analysis curve of poly(*N*-methyl-2-vinylazaborine) (**3**) under a nitrogen atmosphere; sample weight : 7.1430 mg; heating rate: 10.00 K/min; crucible: 40 µL aluminium; T_d: 380 °C (onset); exo up.

Photo

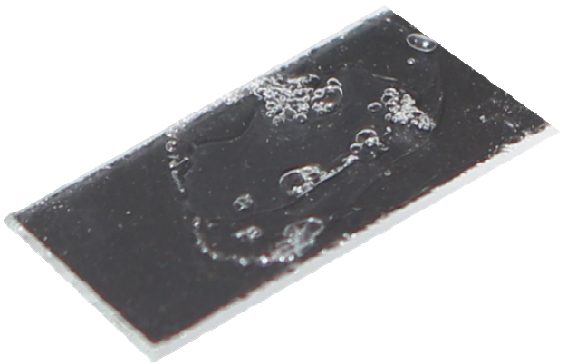
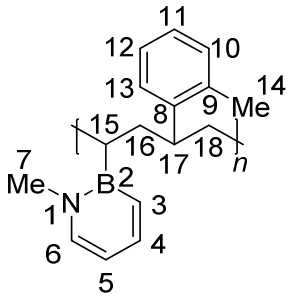


Figure SI- 28. Transparent film of poly(*N*-methyl-2-vinylazaborine) (**3**) on a glass plate after removing the solvent from the dichloromethane solution on a heating plate at 40 °C under inert conditions.

Poly(1-methyl-2-vinylazaborine-2'-methylstyrene) (6)



Under a nitrogen atmosphere, **2** (149 mg. 1.25 mmol), 2-vinyltoluene (148 mg, 1.25 mmol) and AIBN (4 mg, 25 µmol, 1 mol%) were placed into a dried J. Young's tube. The mixture was transferred into a preheated oil bath (85 °C) and stirred for 6 h until it solidified. The polymer was dissolved in a mixture of toluene (2 mL) and diethyl ether (0.5 mL)[p] and precipitated into methanol (6 mL). The polymer was dried under reduced pressure ($4x10^{-2}$ mbar, 40 °C oil bath) to yield poly(1-methyl-2-vinylazaborine-2'-methylstyrene) (**6**) (255 mg, 86%).[q] ^{1}H NMR (600 MHz, C_6D_6) δ 7.82-6.28 (bm, 3/4/5/10/11/12/13-H), 6.29-5.77 (bm, 5-H), 3.35-2.32 (bm, 7/17-H), 2.32-0.51 (bm, 14/15/16/18-H); ^{1}H NMR (600 MHz, CD_2Cl_2) δ 7.66-6.23 (bm, 3/4/5/10/11/12/13-H), 6.23-5.83 (bm, 5-H), 3.32-2.12 (bm, 7/17-H), 2.12-0.39 (bm, 14/15/16/18-H); ^{13}C{^{1}H} NMR (151 MHz, C_6D_6) δ 145.0-144.3 (C-8), 142.2 (C-4), 139.5 (C-6), 136.4 (C-9), 130.6, 129.3, 128.8, 126.4, 125.7 (C-3/10/11/12/13), 110.1 (C-5), 40.5 (C-7), 37.4 (C-15), 35.4 (C-17), 25.9, 24.0 (C-16/18), 19.1 (C-14); ^{13}C{^{1}H} NMR (151 MHz, CD_2Cl_2) δ 145.2-144.5 (C-8), 142.3 (C-4), 139.8 (C-6), 136.6 (C-9), 130.5, 129.6, 128.7, 126.4, 125.8 (C-3/10/11/12/13), 109.9 (C-5), 40.9 (C-7), 36.8 (C-15), 35.0 (C-17), 25.3, 23.9 (C-16/18), 19.0 (C-14); ^{11}B NMR (96 MHz, C_6D_6) δ 35.6, 31.2, 26.7; IR (ATR) ν_{max}/cm^{-1} 3067, 3016, 2946, 2914, 2852, 1612, 1514, 1491, 1459, 1401, 1307, 759, 728, 692, 458; M_W = 36900 g/mol (eluent: THF, elution at 1 mL/min, 35 °C, universal calibration); PDI = 1.68.

[p] Diethyl ether was necessary because the polymer was hardly soluble in pure toluene.
[q] The polymer could not be analysed by mass spectrometry (MALDI, ESI).

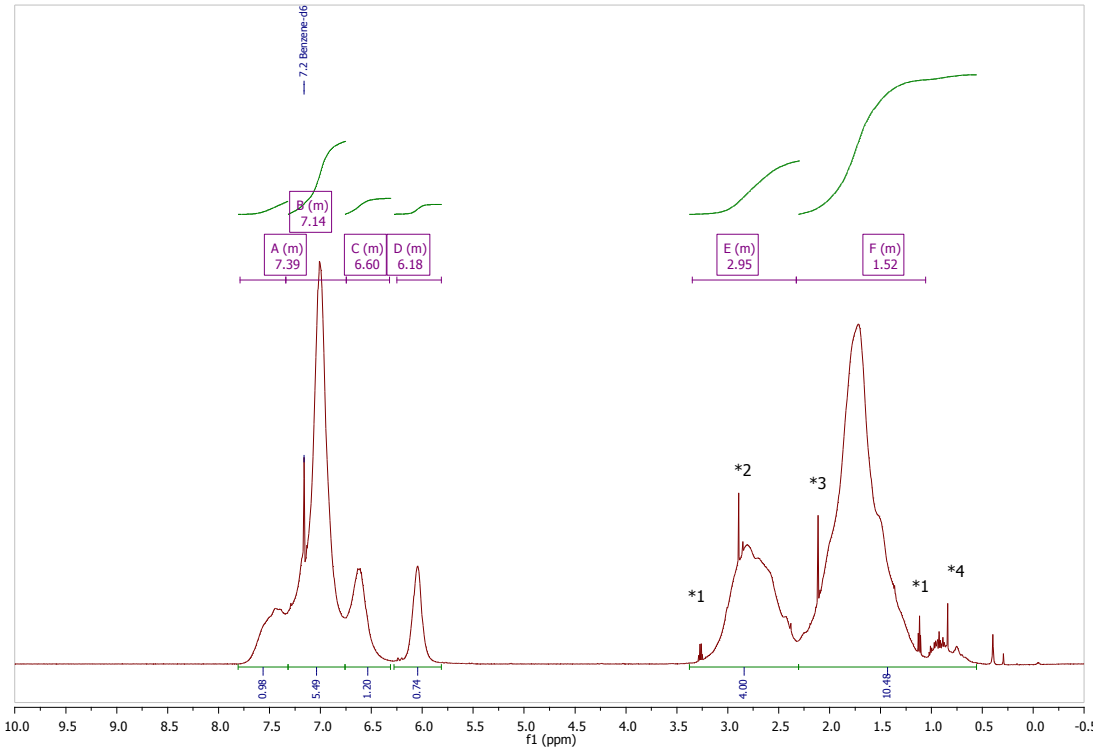


Figure SI- 29. ^{1}H NMR spectrum of the copolymer **6** in C_6D_6; traces from precipitation process: *1 = diethyl ether, *2 = methanol, *3 = toluene.

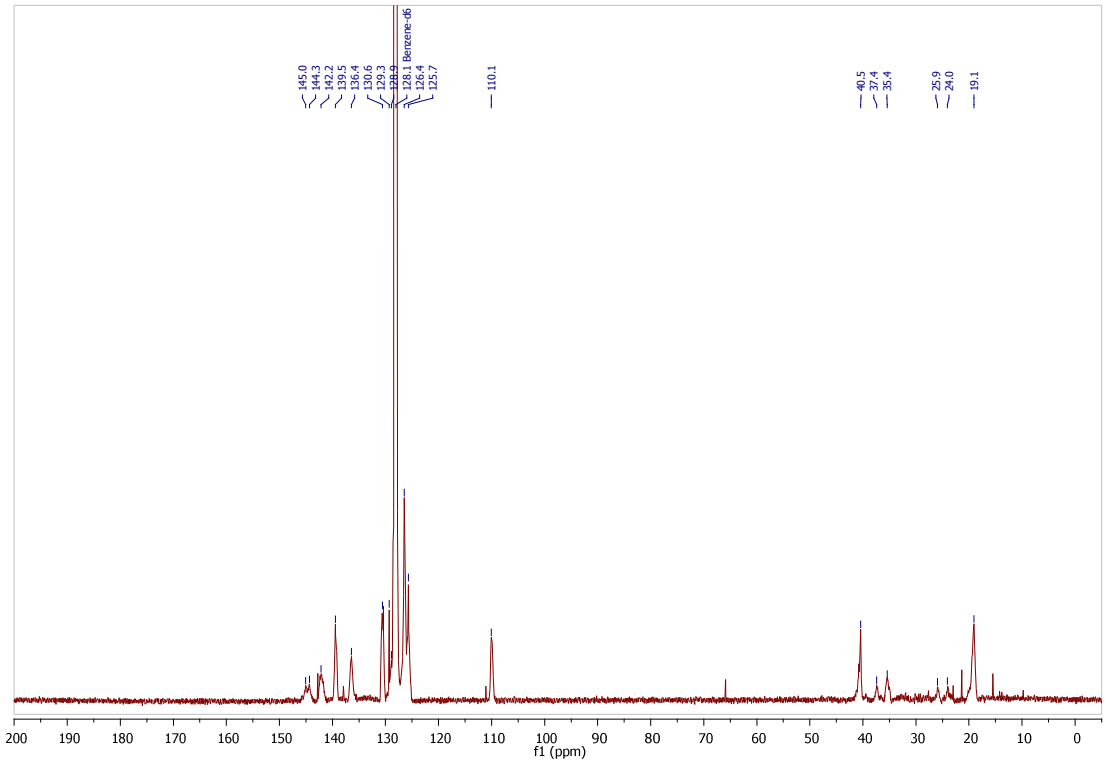


Figure SI- 30. $^{13}C\{^{1}H\}$ NMR spectrum of copolymer **6** in C_6D_6.

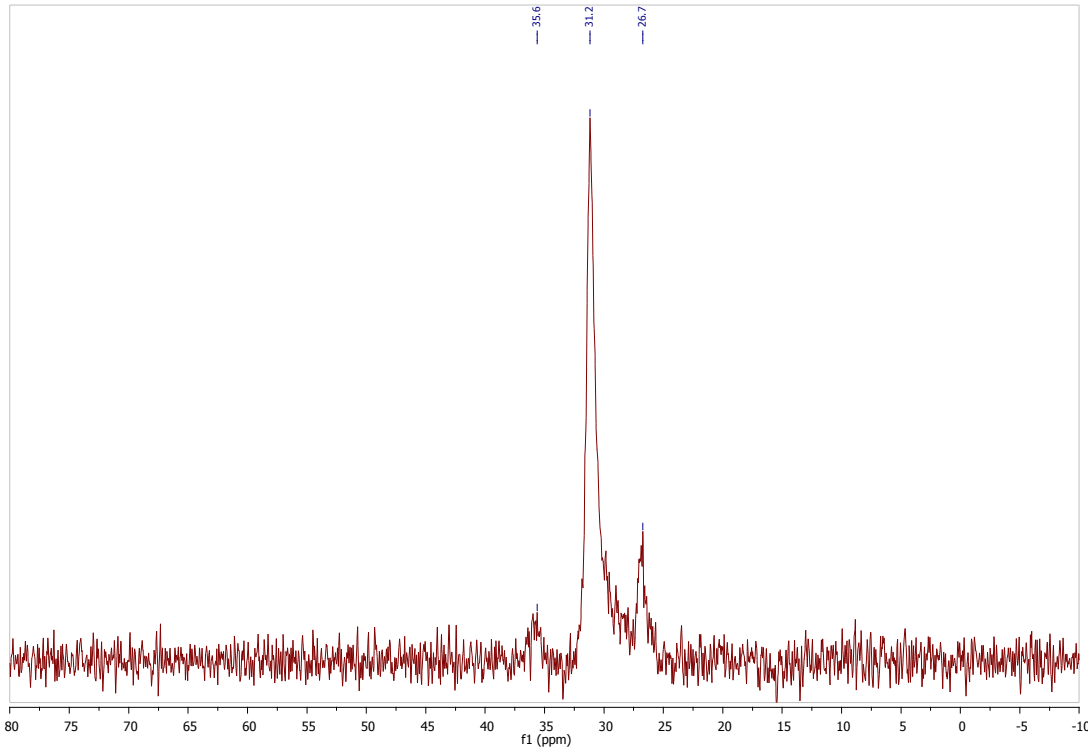


Figure SI- 31. ^{11}B NMR spectrum of copolymer **6** in C_6D_6.

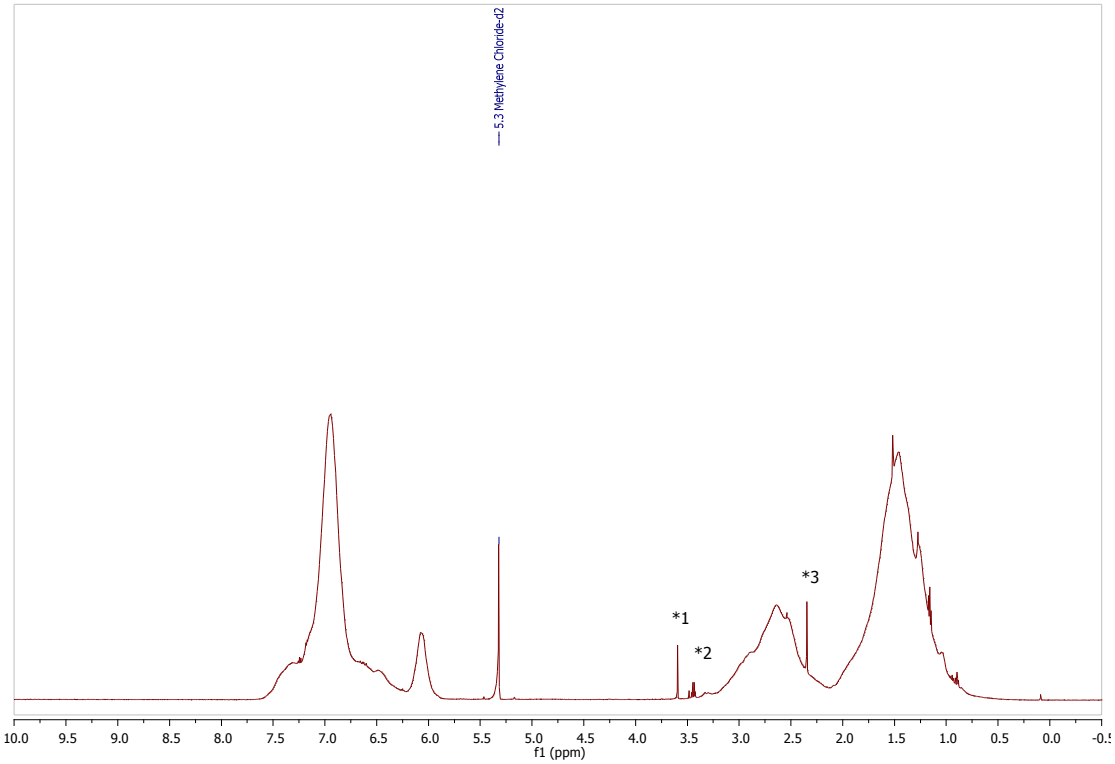


Figure SI- 32. ^{1}H NMR spectrum of copolymer **6** in CD_2Cl_2; traces from precipitation process: *1 = monomer, *2 = diethyl ether, *3 = monomer/toluene.

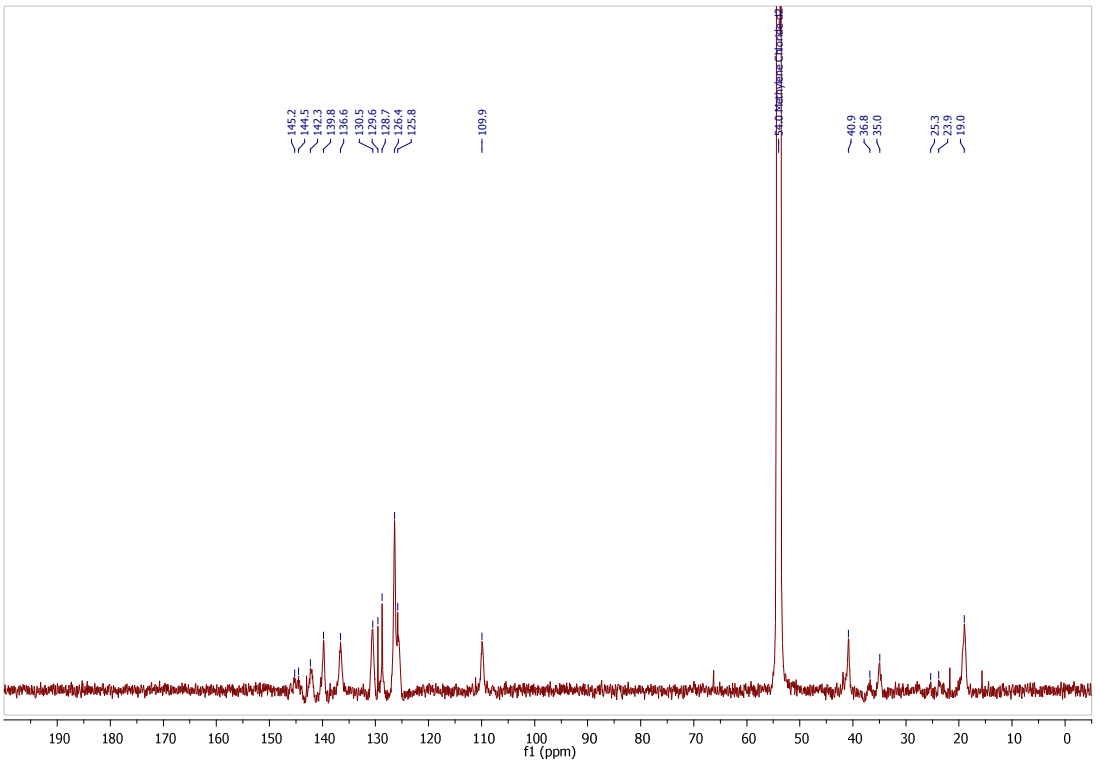


Figure SI- 33. $^{13}C\{^{1}H\}$ NMR spectrum of copolymer **6** in CD_2Cl_2.

Table SI- 3. GPC results for the copolymer **6** measured in THF; Conventional calibration was performed with polystyrene standards (narrow distribution) and a refractive index detector; Universal calibration was performed with additional on-line viscometer detection.

	Conventional Calibration	**Universal Calibration**
Mn (g/mol)	12100	21900
Mw (g/mol)	22800	36900
PDI	1.88	1.68

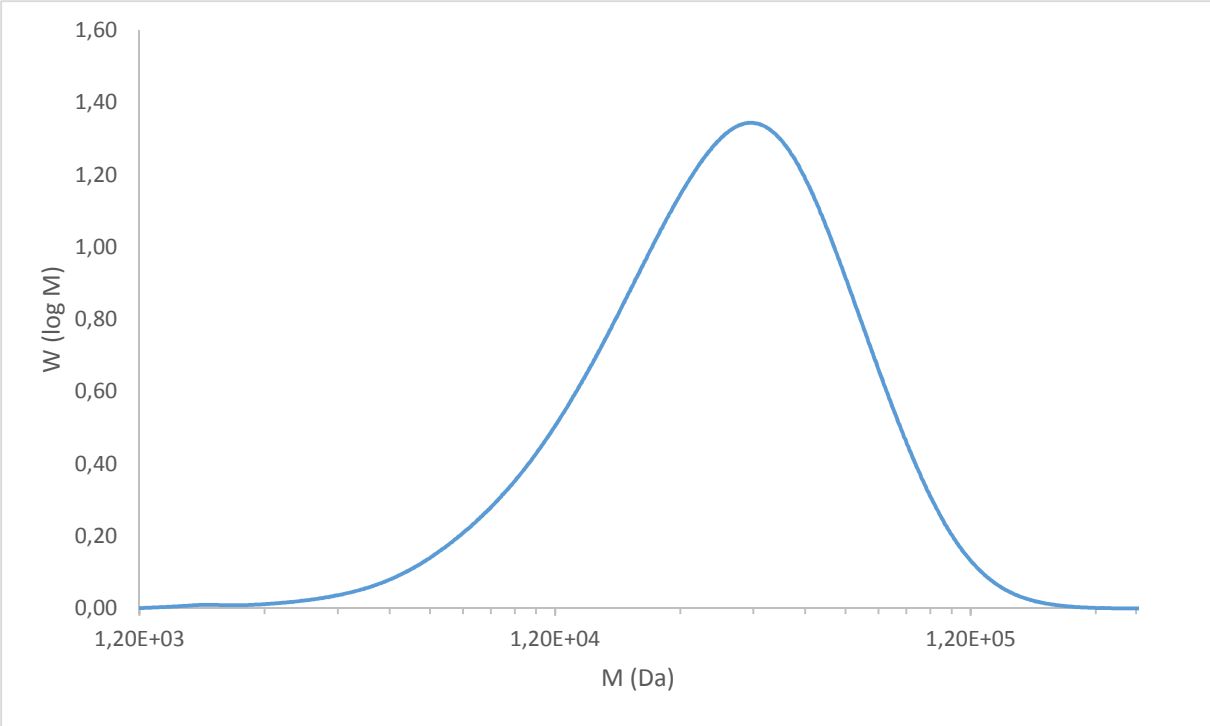


Figure SI- 34. Mass distribution curve of copolymer **6** (universal calibration) measured in THF.

DSC

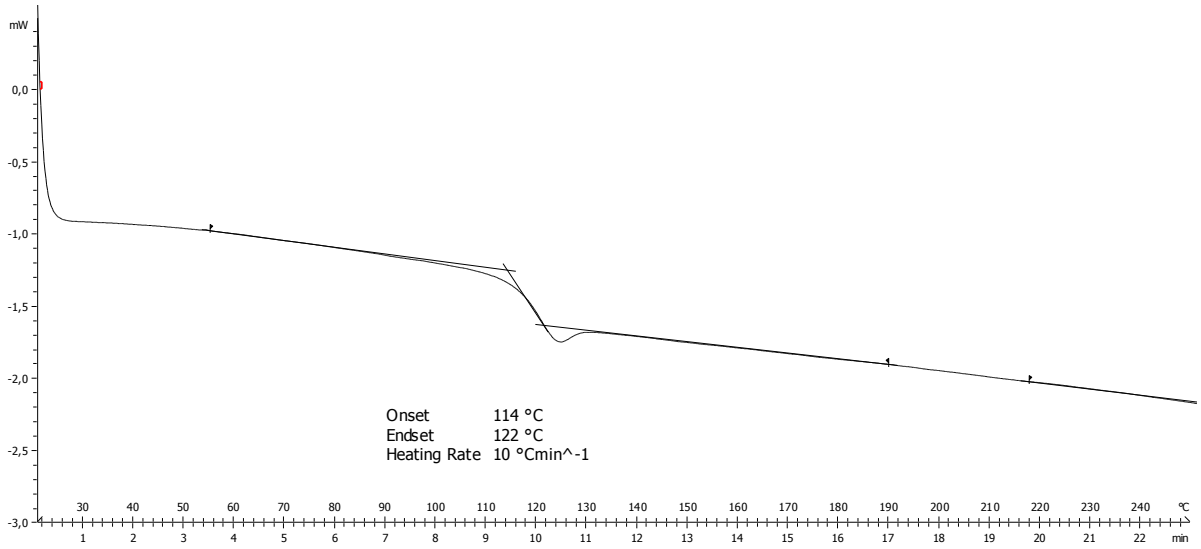


Figure SI- 35. Differential scanning calorimetry curve of copolymer **6** under a nitrogen atmosphere; sample weight: 8.4226 mg; heating rate: 10 K/min; crucible: 40 µL aluminium; T_g: 114 °C (onset); exo up.

TGA

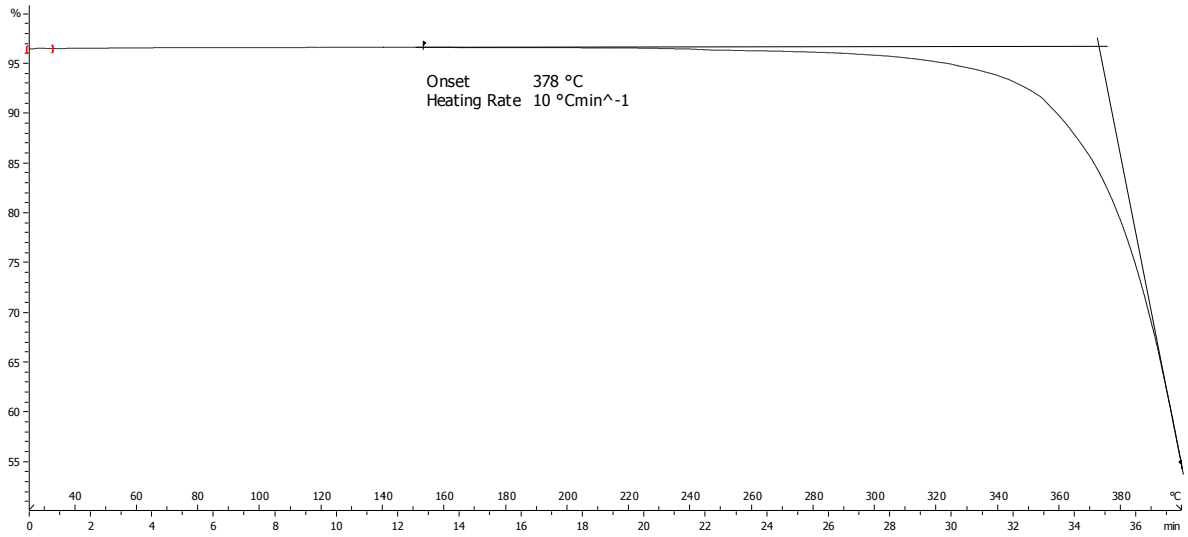
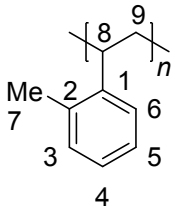


Figure SI- 36. Thermogravimetric analysis curve of copolymer **6** under nitrogen atmosphere; sample weight: 11.5770 mg; heating rate: 10 K/min; crucible: 40 µL aluminium; T_d: 378 °C (onset).

Photo

Figure SI- 37. Transparent film of copolymer **6** on a glass plate after removing the solvent from the dichloromethane solution at 40 °C under inert conditions.

Poly(2-methylstyrene) (4)



Under a nitrogen atmosphere, 2-vinyltoluene (306 mg. 2.5 mmol) and AIBN (4 mg, 25 µmol, 1 mol%) were placed into a dried J. Young's tube. The mixture was transferred into a preheated oil bath (85 °C). After 4 h of heating, the mixture solidified. The solid polymer was purified by precipitation: it was dissolved in a mixture of toluene (2 mL) and ethyl acetate (0.5 mL)[r] and afterwards precipitated into methanol (6 mL). The polymer was dried under reduced pressure ($4x10^{-2}$ mbar, 40 °C oil bath) to yield poly(2-methylstyrene) (**4**) (265 mg, 87%)[s] ^{1}H NMR (600 MHz, C_6D_6) δ 7.5-6.4 (4 H, bm, 3,4,5,6-H), 2.9-2.3 (1 H, bm, 8-H), 2.2-1.1 (5 H, bm, 7,9-H); ^{1}H NMR (500 MHz, CD_2Cl_2) δ 7.4-6.25 (4 H, bm, 3,4,5,6-H), 2.8-2.1 (1 H, bm, 8-H), 2.1-0.9 (5 H, bm, 7,9-H); ^{13}C{^{1}H} NMR (151 MHz, C_6D_6) δ 144.1 (C-1), 136.6 (C-2), 130.8, 126.5, 126.0, 125.7 (C-3/4/5/6), 46.2-40.8 (C-8)[t], 35.1 (C-9), 19.1 (C-7); ^{13}C{^{1}H} NMR (126 MHz, CD_2Cl_2) δ 143.7 (C-1), 136.6 (C-2), 130.6, 126.3, 125.8, 125.6 (C-3/4/5/6), 47.5-41.6 (C-8)[u], 34.7 (C-9), 28.8 (C-7); IR (ATR) ν_{max}/cm^{-1} 3067, 3020, 2950, 2910, 2856, 1487, 1455, 755, 728, 452; M_W = 86000 g/mol (eluent: THF, elution at 1 mL/min, 35 °C, universal calibration); PDI = 1.84.

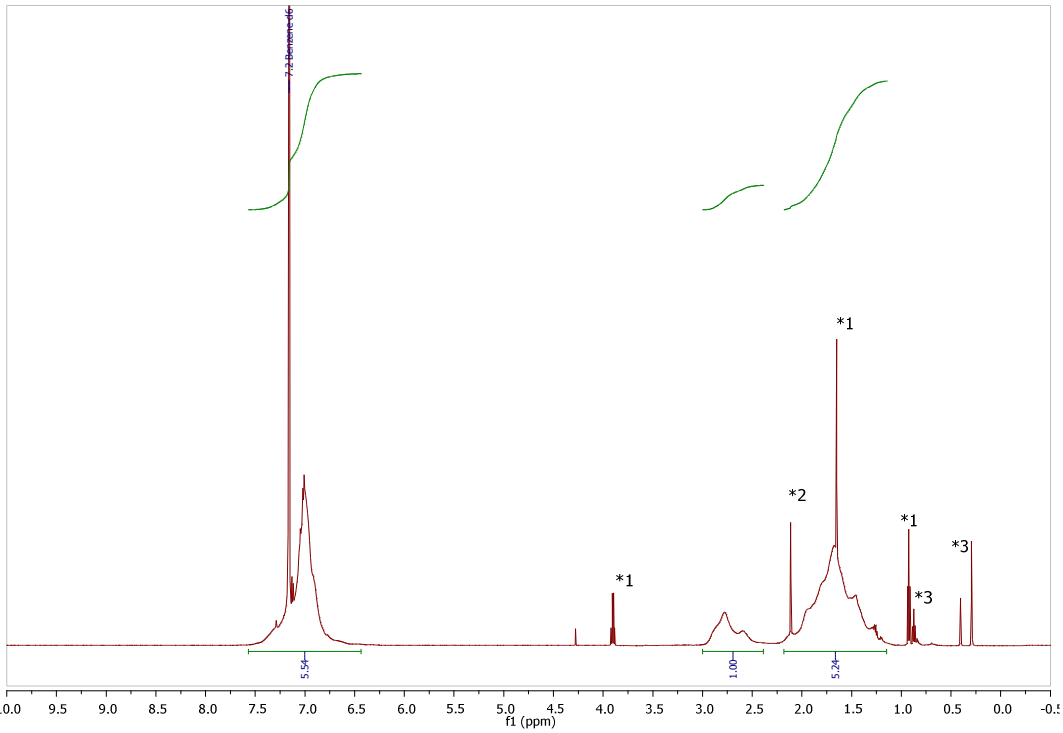


Figure SI- 38. ^{1}H NMR spectrum of polymer **4** in C_6D_6; trace impurities from the work-up process: *1 = ethyl acetate, *2 = toluene, *3 = unidentified signal.

[r] Ethyl acetate was necessary because the polymer was poorly soluble in pure toluene.
[s] The polymer could not be analysed by mass spectrometry (MALDI, ESI).
[t] The signal is only visible in the HSQC spectrum (possibly too broad).
[u] The signal is only visible in the HSQC spectrum (possibly too broad).

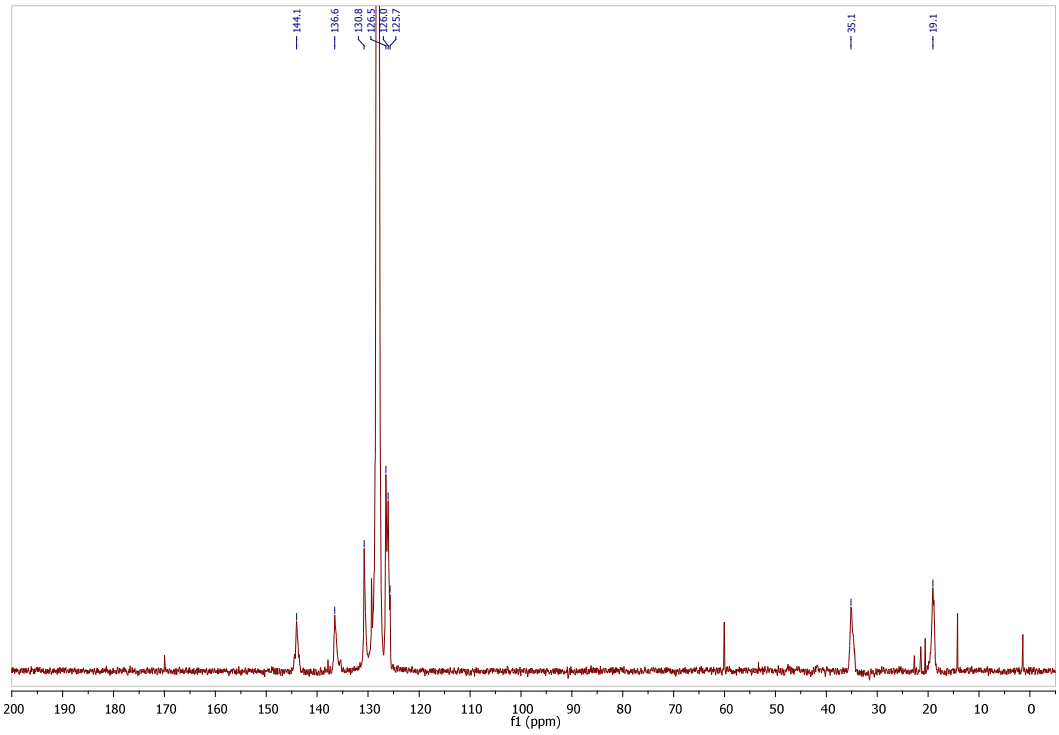


Figure SI- 39. $^{13}C\{^{1}H\}$ NMR spectrum of polymer **4** in C_6D_6.

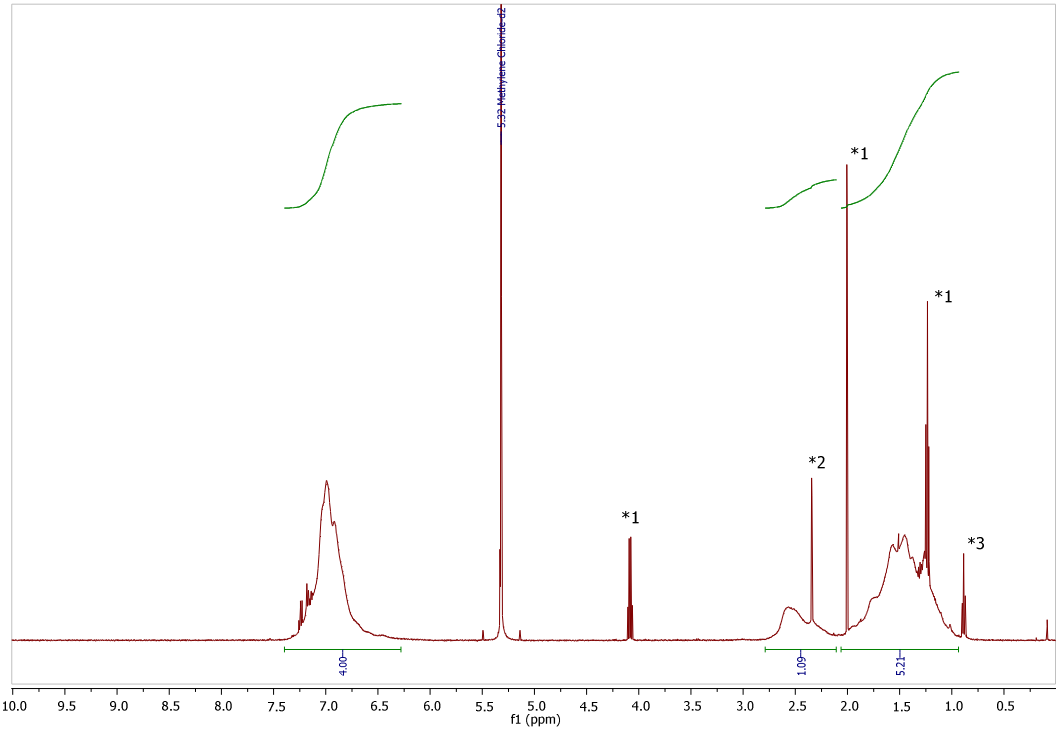


Figure SI- 40. ^{1}H NMR spectrum of polymer **4** in CD_2Cl_2; traces from precipitation process: *1 = ethyl acetate, *2 = methanol, *3 = toluene.

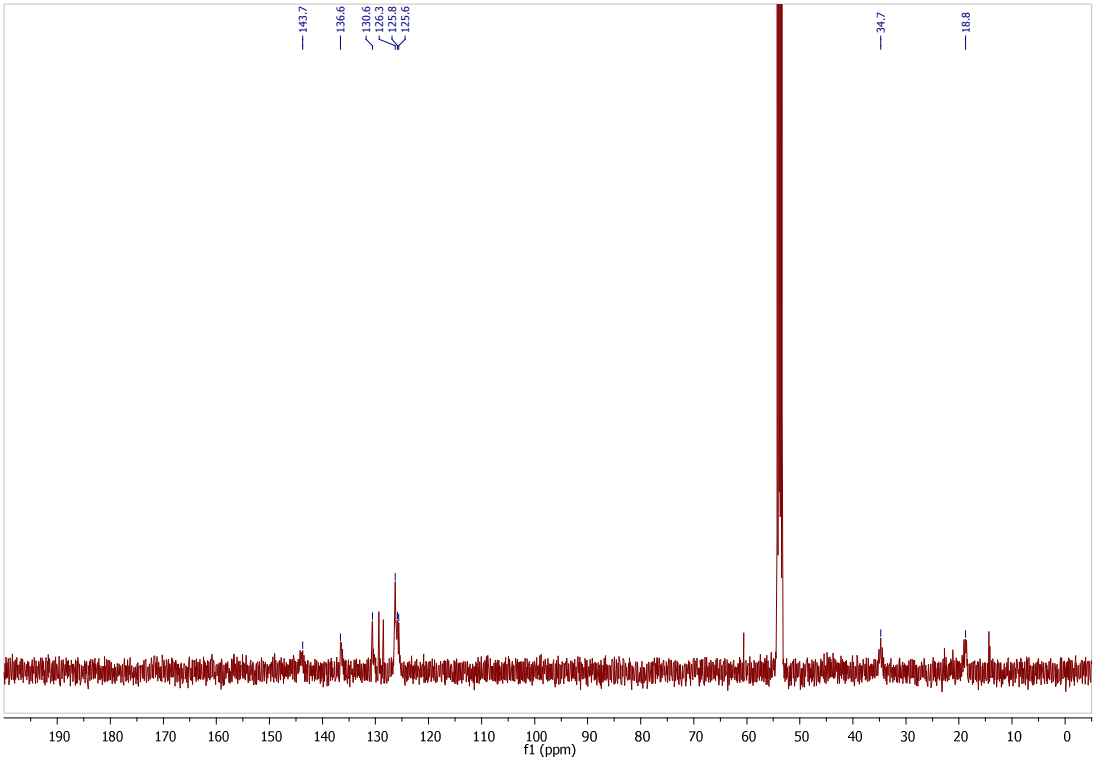


Figure SI- 41. $^{13}C\{^{1}H\}$ NMR spectrum of polymer **4** in CD_2Cl_2.

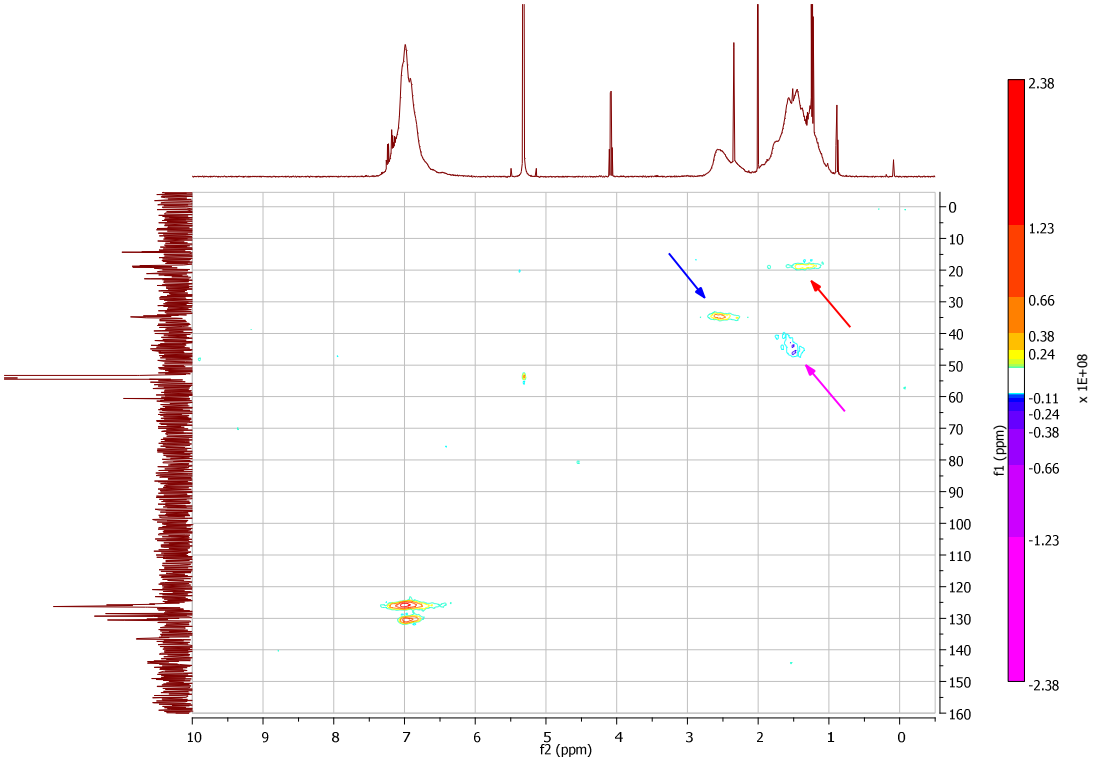


Figure SI- 42. HSQC-DEPT experiment in CD_2Cl_2 for assigning the ^{1}H and ^{13}C signals of polymer **4**. The signal for the *N*-methyl groups are clearly visible (red arrow); In the signal for the olefinic backbone, there is a signal for a methylene group (purple arrow) and a further signal for the CH-group (blue arrow). There is no evidence that the *N*-methyl group has reacted during the radical polymerization.

Table SI- 4. GPC results of poly(2-methylstyrene) (**4**) measured in THF; Conventional calibration was performed with polystyrene standards (narrow distribution) and a refractive index detector; Universal calibration was performed with additional on-line viscometer detection.

	Conventional Calibration	**Universal Calibration**
Mn (g/mol)	25900	46700
Mw (g/mol)	59800	86000
PDI	2.31	1.84

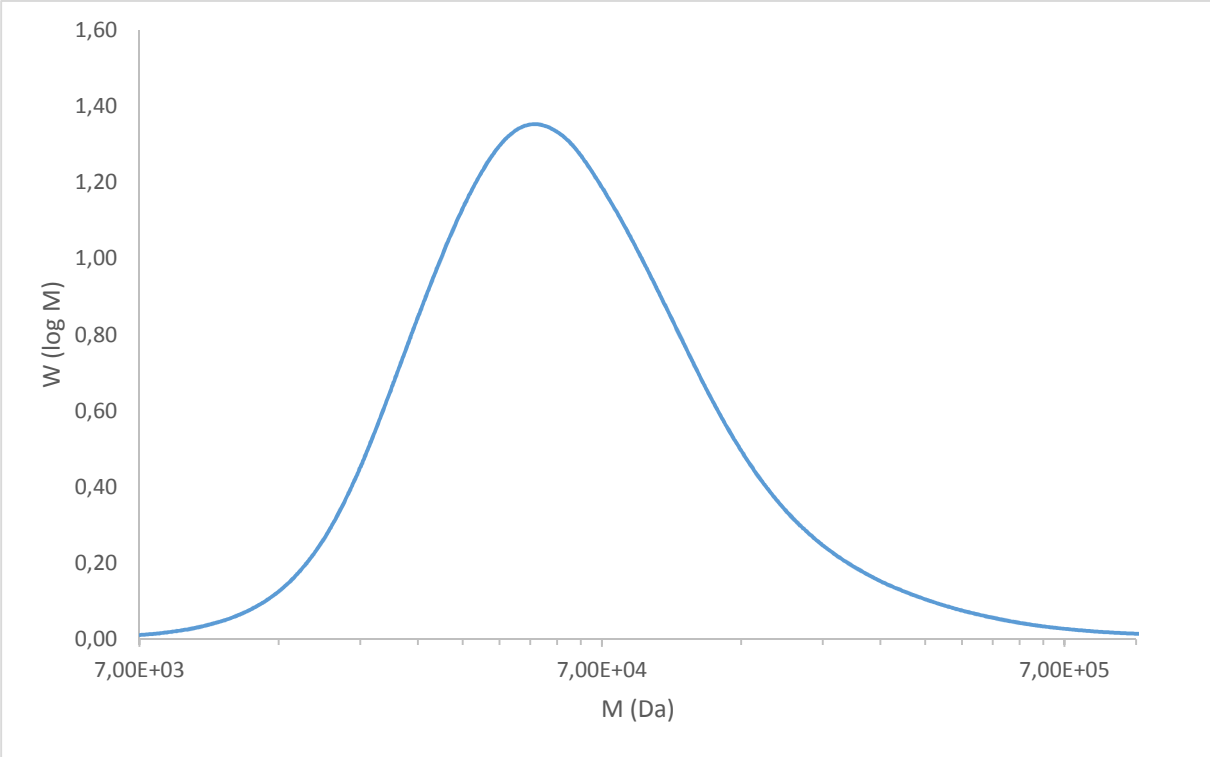


Figure SI- 43. Mass distribution curve of poly(2-methylstyrene) (**4**) (universal calibration) measured in THF.

DSC

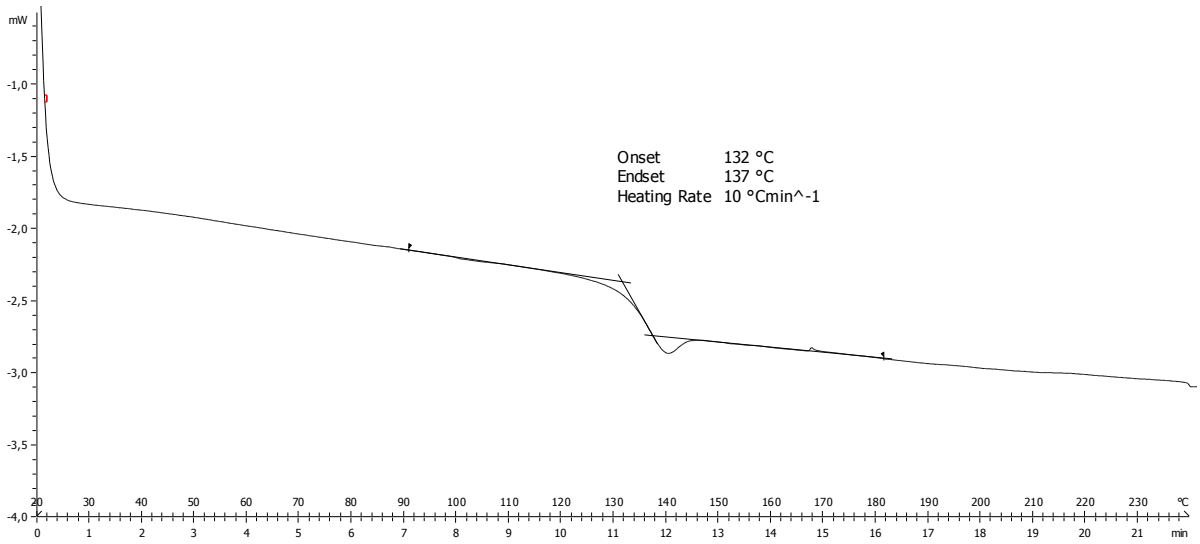


Figure SI- 44. Differential scanning calorimetry curve of poly(2-methylstyrene) (**4**) under a nitrogen atmosphere; sample weight: 8.2736 mg; heating rate: 10 K/min; crucible: 40 µL aluminium; T_g: 132 °C (onset); exo up.

TGA

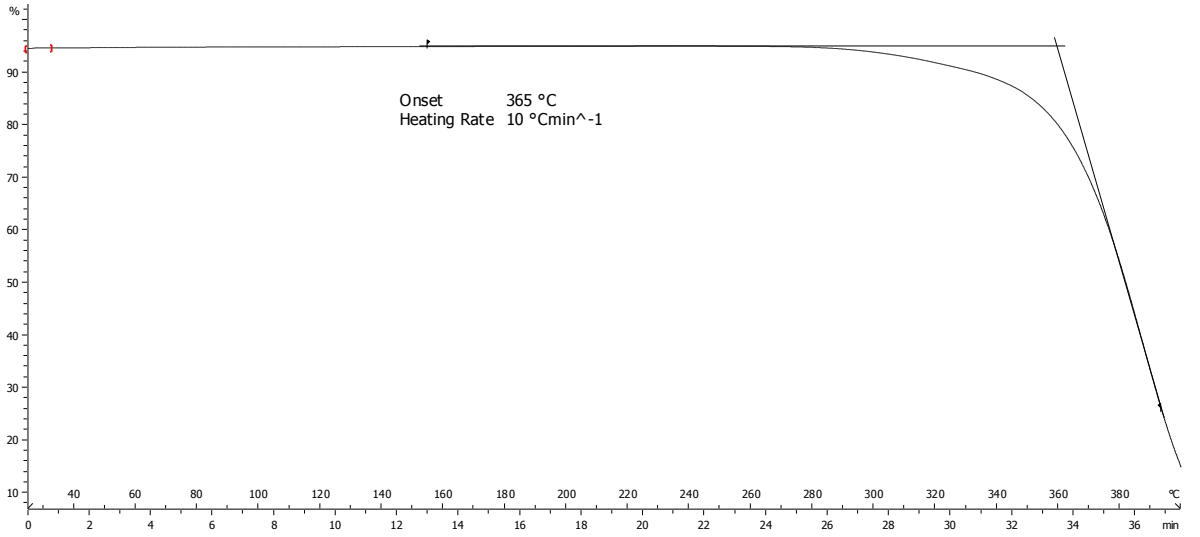


Figure SI- 45. Thermogravimetric analysis curve of poly(2-methylstyrene) (**4**) under a nitrogen atmosphere; sample weight: 7.1067 mg; heating rate: 10 K/min; crucible: 40 µL aluminium; T_d: 365 °C (onset).

Additional Comparisons

^{1}H NMR comparison

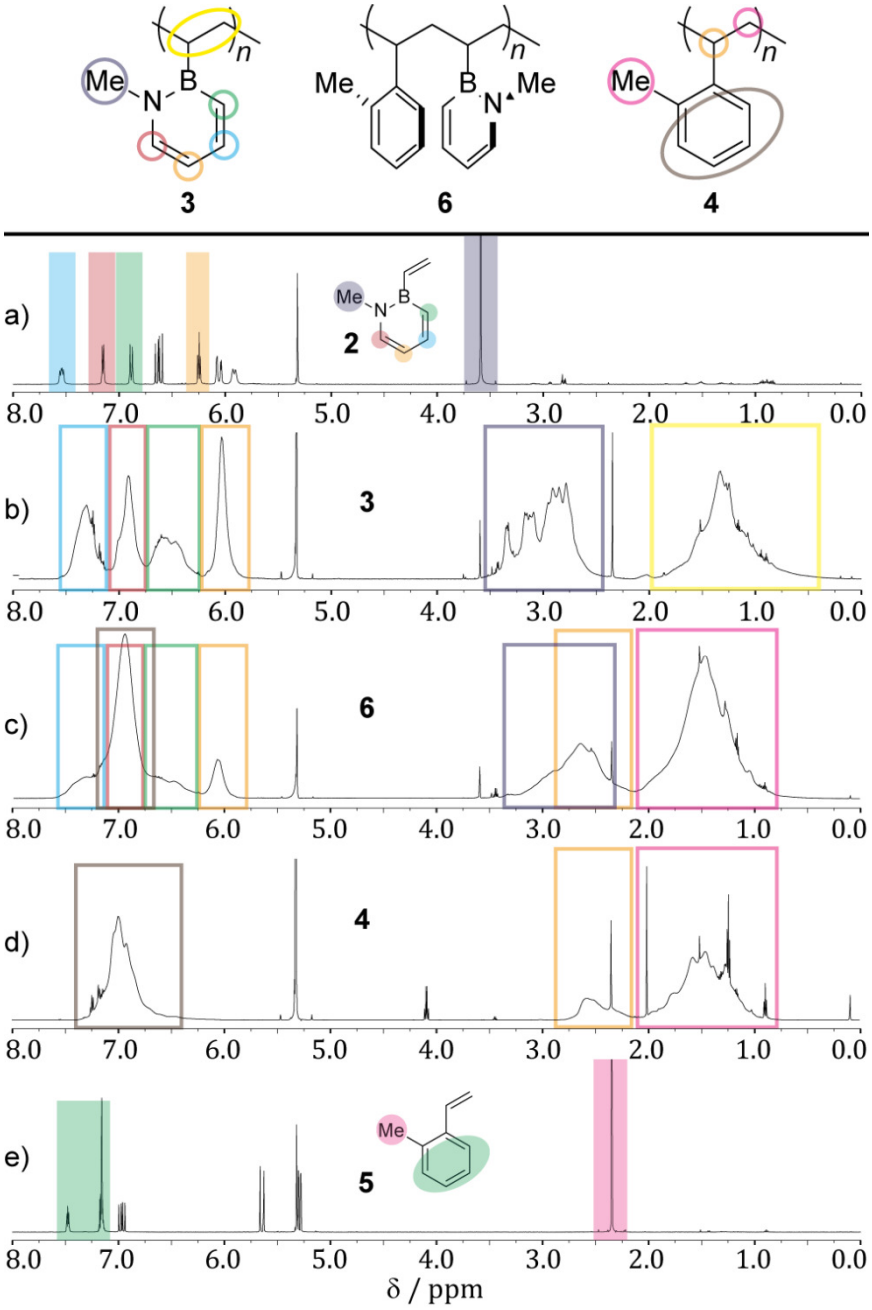


Figure SI- 46. ^{1}H NMR comparison with signal assignment of all polymers.

$^{13}C\{^{1}H\}$ NMR comparison

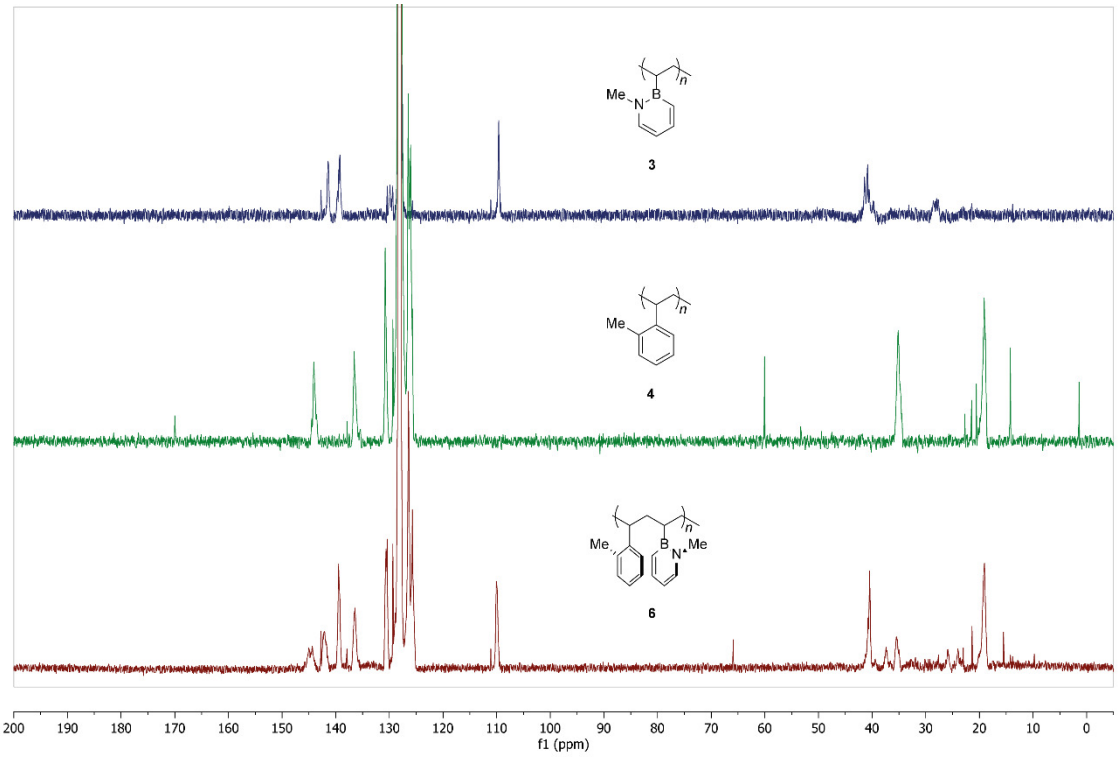


Figure SI- 47. Stacked $^{13}C\{^{1}H\}$ NMR spectra of all three synthesized polymers in C_6D_6.

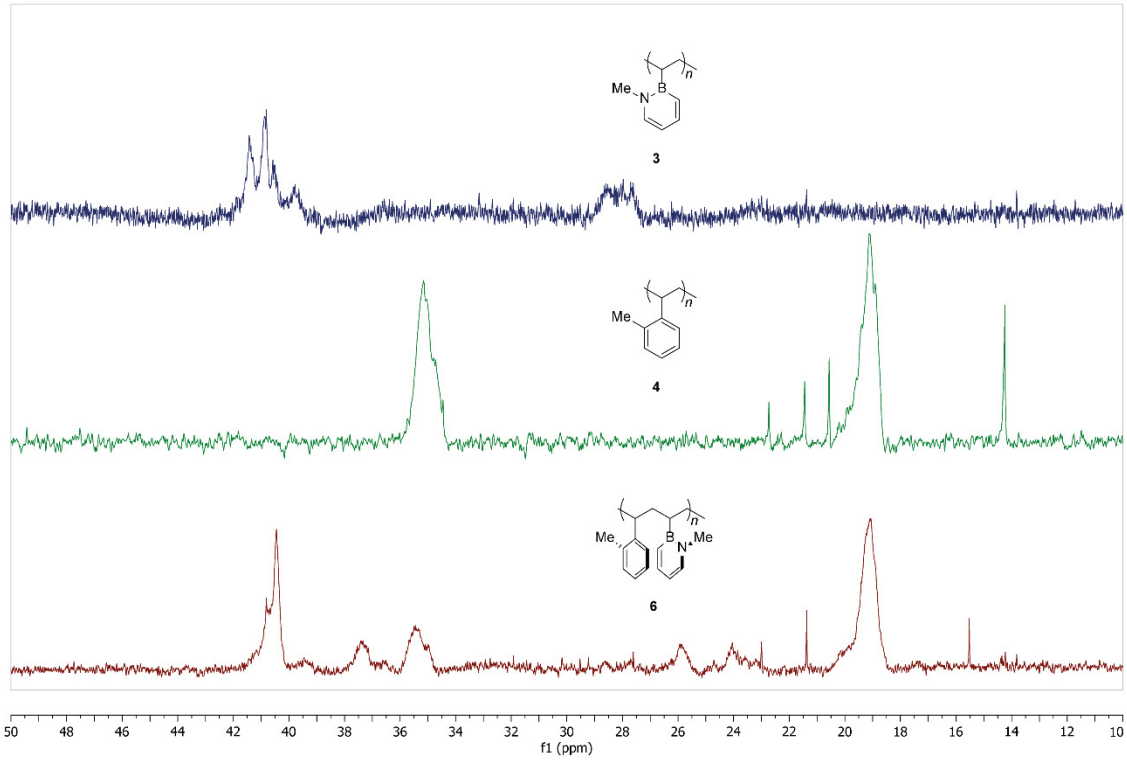


Figure SI- 48. Section of the aliphatic range of the stacked $^{13}C\{^{1}H\}$ NMR of all three synthesized polymers in C_6D_6.

IR comparison

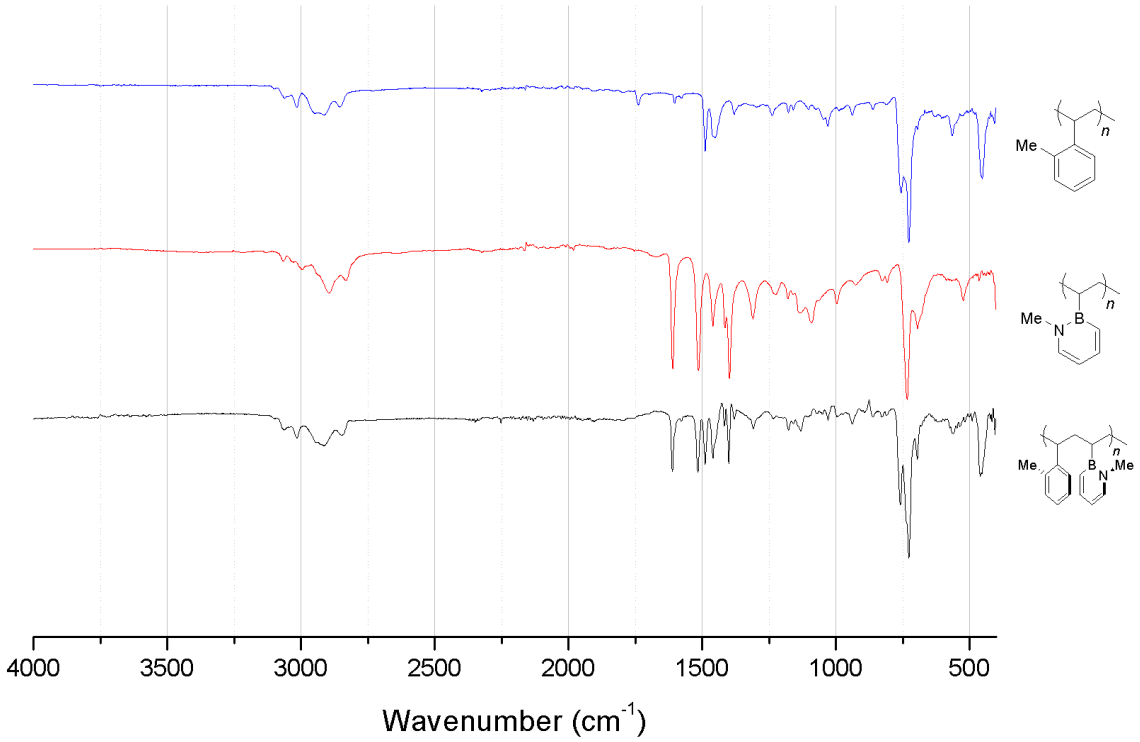


Figure SI- 49. Stacked IR spectra of the homopolymers **3**, **4** and copolymer **6**.

UV-vis comparison

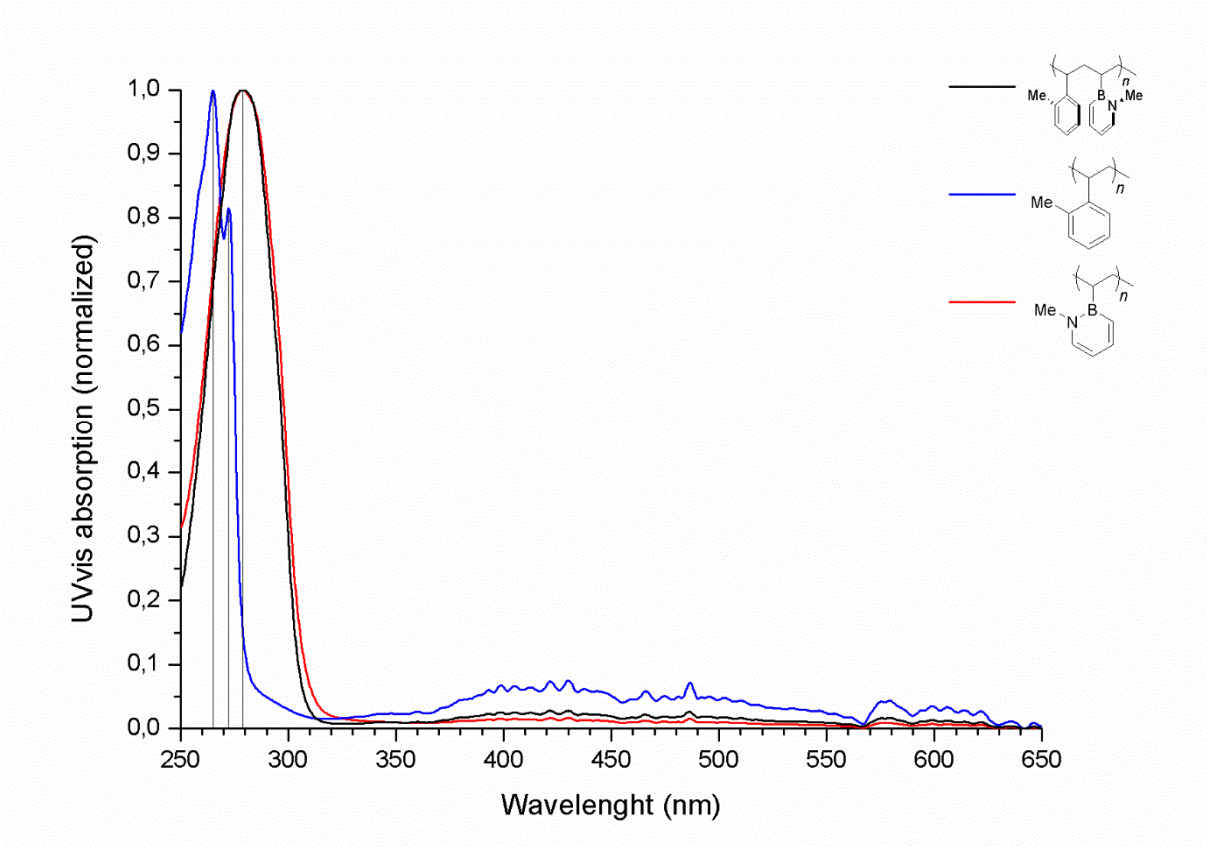


Figure SI- 50. UV-vis spectrum of all three polymers directly from GPC measurements in THF. Maxima: 279 (**6**, black); 265, 273 (**4**, blue); 279 (**3**, red) nm.

Kinetic measurements (monomer conversion control by ^{1}H NMR)

Monomer conversions were calculated using proton integrals of both separated monomer and polymer signals. The reactions were set up as described for the synthesis for isolation with same scale in a glovebox (see above). Then, at regular intervals, samples were obtained by taking a drop of the mixture with a pipette and diluted it with CD_2Cl_2 into a J. Young's NMR tube, before ^{1}H NMR spectra were measured.

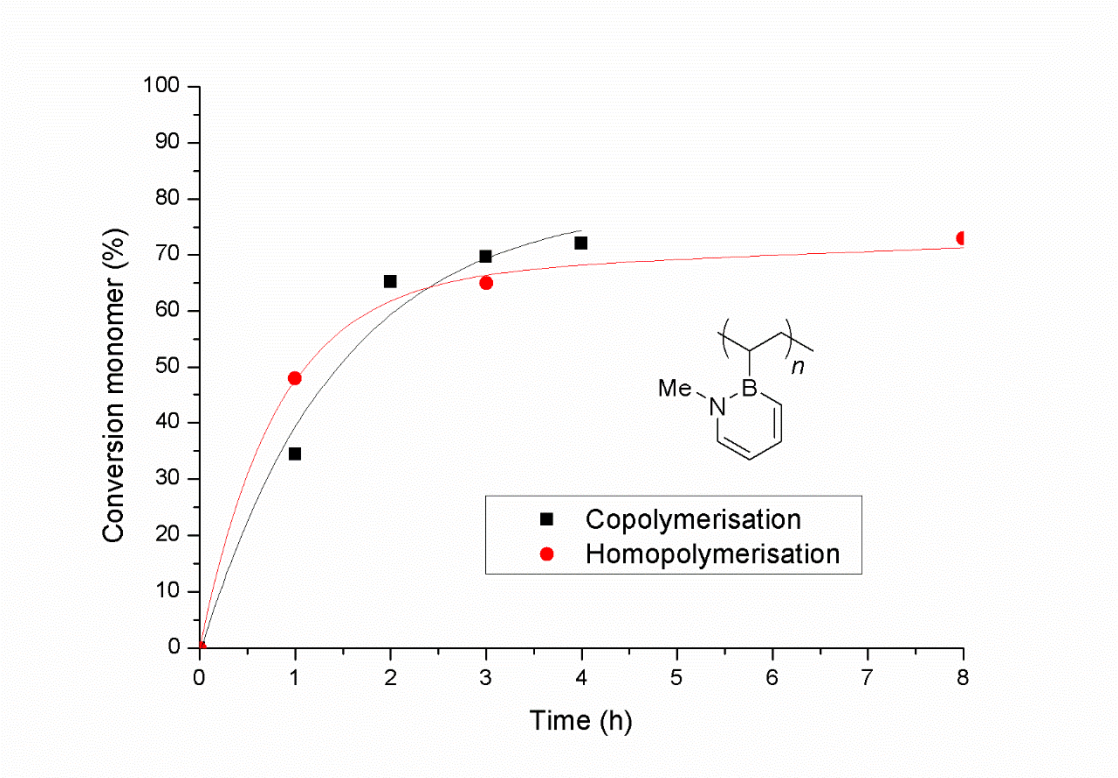


Figure SI- 51. Monomer conversion of polymerizing *N*-methyl-2-vinylazaborine (**2**).

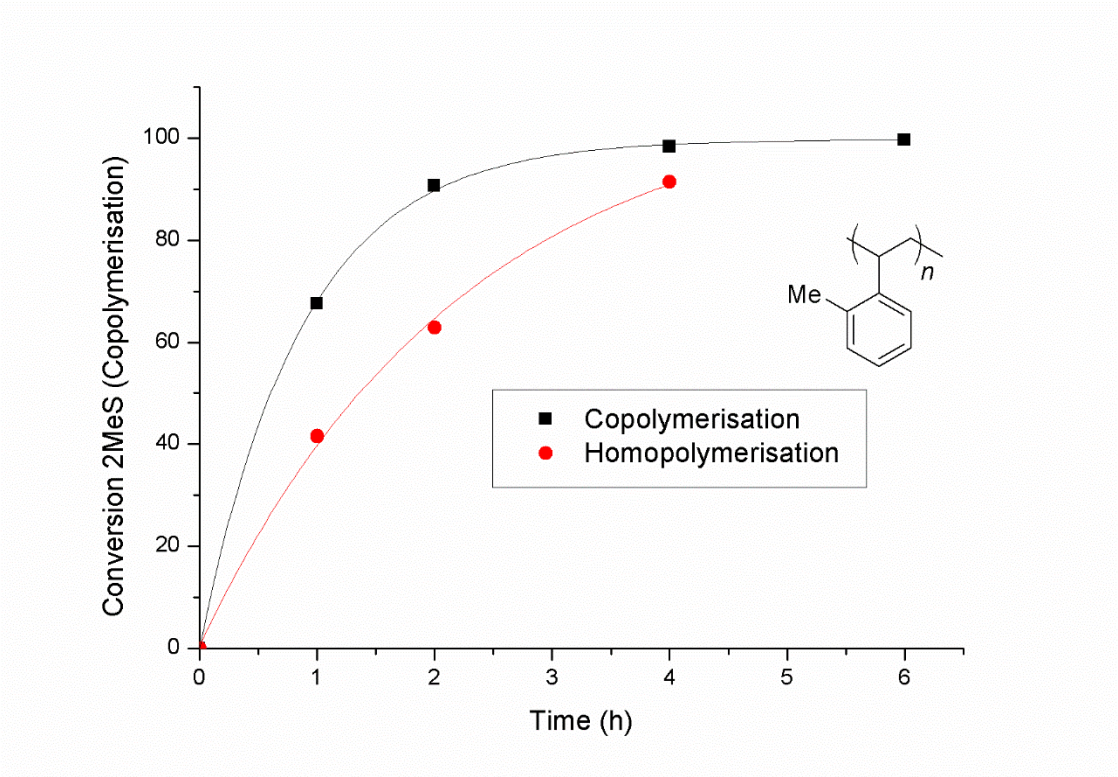


Figure SI- 52. Monomer conversion of polymerizing 2-methylstyrene (**5**).

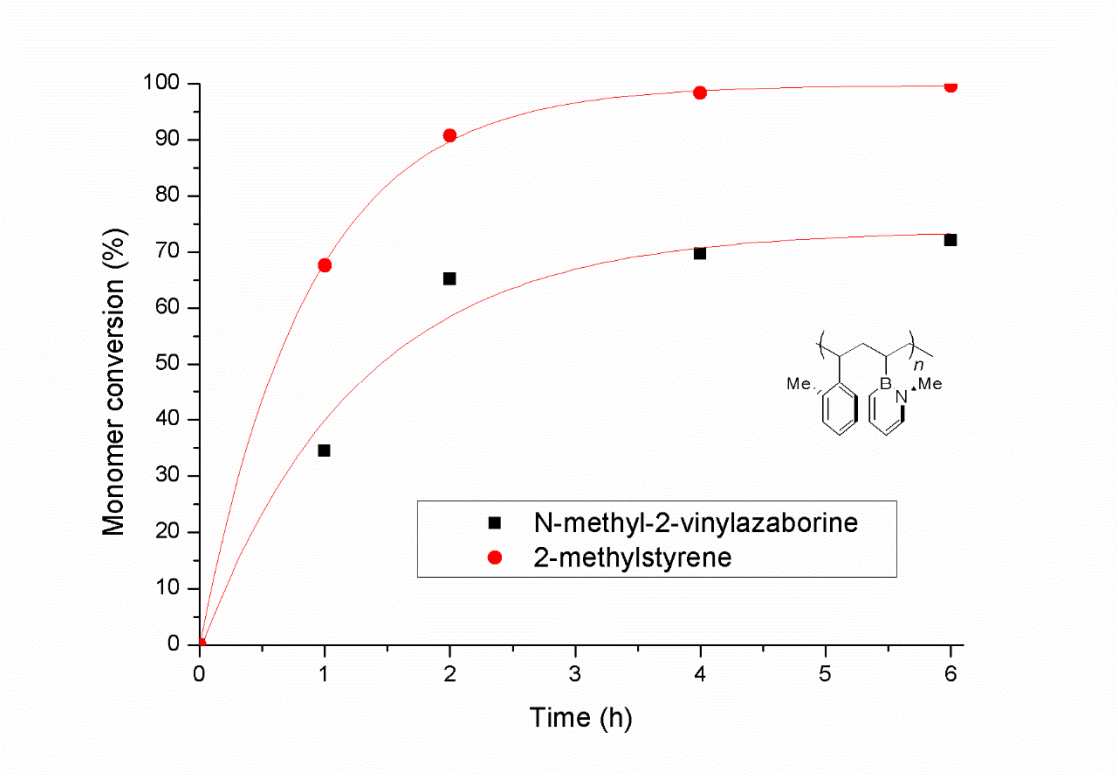
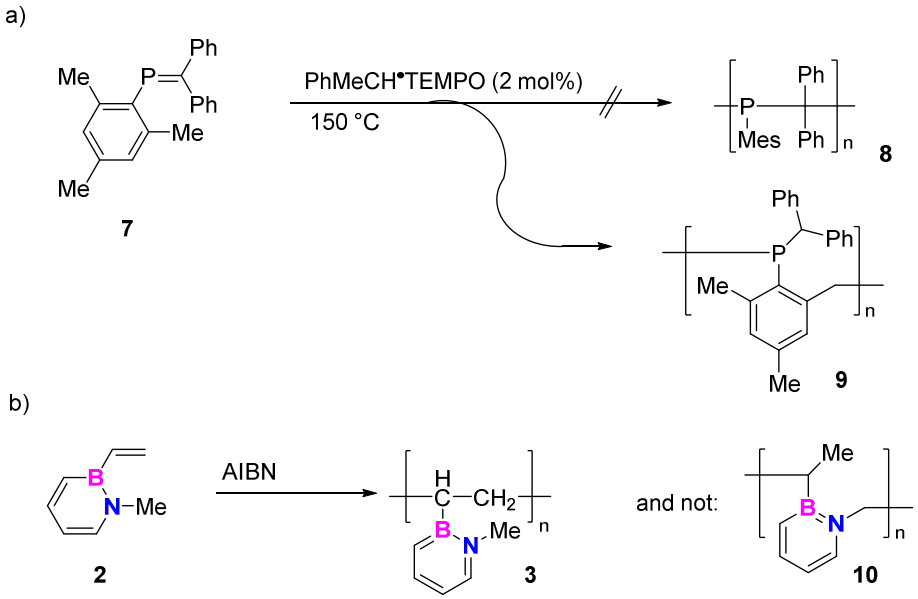


Figure SI- 53. Monomer conversions of N-methyl-2-vinylazaborine (**2**) and 2-methylstyrene (**5**) while copolymerization to polymer **6**.

Discussion of a Possible Involvement of the *N*-Methyl Group in the Polymerization

Recent work by Gates and co-workers is concerned with a phosphoros analog of alkenes that could be polymerized under radical conditions.[8-11] A detailed analysis of the structure of the product revealed an intriguing structure of the polymer prepared by radical polymerization (**Scheme SI-1**).[12] Rather than observing a polymer chain obtained by a normal addition polymerisation (**8**), the authors found that the methyl group in *ortho* position of the mesityl group on the phosphorus was not innocent. Instead an isomerization polymerization was observed, leading to polymer **9**.



Scheme SI- 1. a) Isomerization polymerization of the phosphaalkene MesP=CPh_2. b) Comparison with the polymerization of the azaborine **2** to give the polymer **10** was not observed.

Although the *N*-methyl group for the N-methylazaborine **2** is topologically in the same position, we found no evidence of the occurrence of **10**. Firstly, the methyl group in **10** should be quite distinctive from that in **3** by an upfield shift as it is no longer under the shielding influence of the nitrogen. This is not the case; the methyl groups appear between ca. 2.5 to 3.5 ppm (in CD_2Cl_2). In this region of the spectrum, we would then expect a methylene group for **10**. The HSQC-DEPT experiment however (**Figure SI-23**) shows no such signal whatsoever.

The integrations of the peaks are naturally imprecise due to their broadness and also due to remaining trace impurities. However, all other NMR experiments that were performed uniformly support the hypothesis that **3** was formed.

Polymer **9** remains a unique phenomenon.

Abbreviations

FPT	Freeze, Pump & Thaw
Et_3N	Triethylamine
CH_2Cl_2	Dichloromethane
CD_2Cl_2	Deuterated dichloromethane
C_6D_6	Deuterated benzene
Et_2O	Diethyl ether
IR	Infrared spectroscopy
NMR	Nuclear magnetic resonance spectroscopy
Pd	Palladium
T_g	Glass transition temperature
T_d	Decomposition temperature

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