Supporting Information

Allyl Borates: A Novel Class of Polyhomologation Initiators

De Wang, Nikos Hadjichristidis*

King Abdullah University of Science and Technology (KAUST), Physical Sciences and Engineering Division, KAUST Catalysis Center, Polymer Synthesis Laboratory, Thuwal 23955, Kingdom of Saudi Arabia
E-mail: nikolaos.hadjichristidis@kaust.edu.sa

Experiment Section

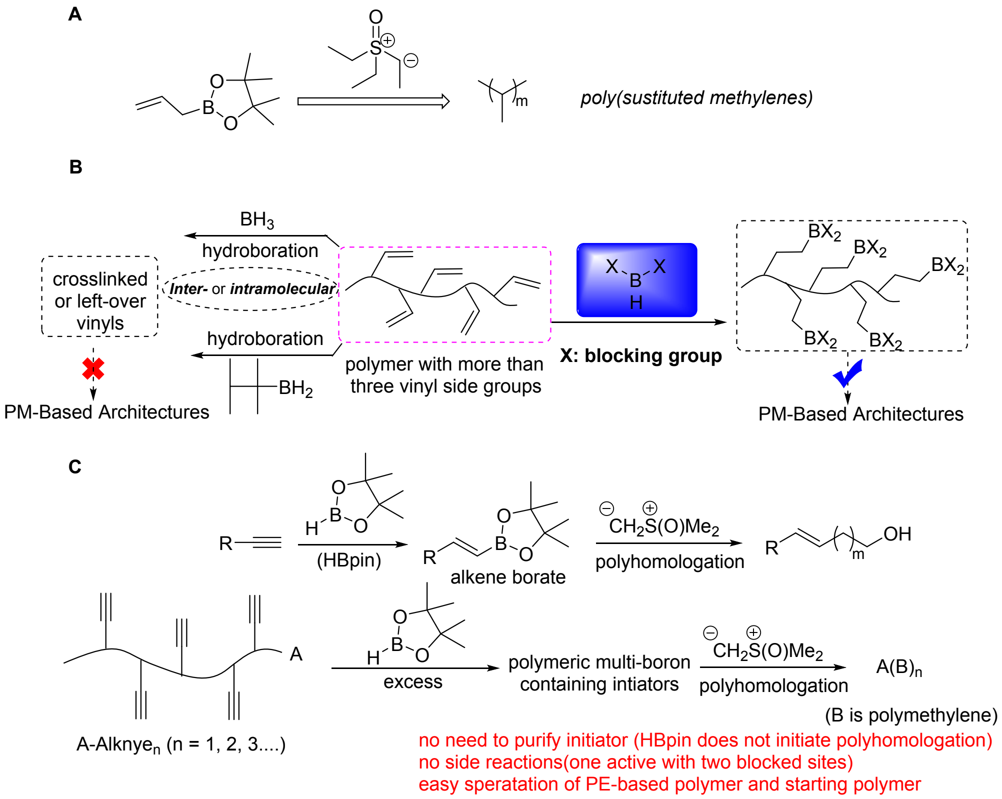
Instruments:

High temperature size exclusion chromatography (HT-SEC) measurements were carried out on a Viscoteck HT-GPC module 350 instrument with two PLgel 10 μm MIXED-B columns, using 1,2,4-trichlorobenzene (TCB) as eluent at a flow rate of 0.8 mL/min at 150 ºC or on an Agilent PL-GPC 220 with one PLgel 10 μm MIXED-B column using TCB as eluent at a flow rate of 1.0 mL/min at 150 ºC. Both systems were calibrated by versus PS standards. The ^{1}H NMR spectra were recorded with a Bruker AVANCE III-500 or 600 spectrometer. ^{11}B NMR spectra were recorded with a Bruker AVANCE III-600 spectrometer.

Materials

Benzyltri-*n*-butylammonium chloride (98%, Alfa Aesar) and trimethylamine N-oxide dihydrate (TAO) (>99%, Fluka) were used as received. Sodium hydride (60% dispersion in mineral oil, Acros) was washed with petroleum ether (40-60 ºC) prior to use. Methanol (99%, Fisher), dichloromethane (>99%, Fisher) were obtained from Fisher and used as received. Tetrahydrofuran (99%, Fisher) and toluene (99.7%, Fluka) were distilled from sodium prior to use. Initiator **2** used in this paper either bought from Aldrich or synthesized follow the literature.[1] The initiator bought from Aldrich was distilled one time prior to use.

The advantages of the monofunctional borate initiators

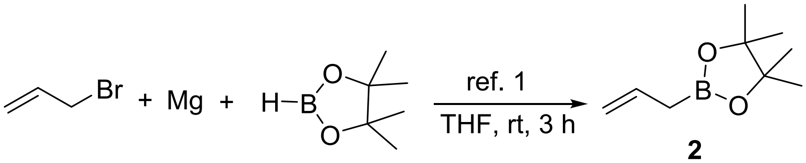


Scheme S1 The advantage of a monofunctional compared to the di- and trifunctional hydroboration initiators precursors towards the synthesis of well-defined PM-based complex macromolecular architectures

Until now borane (trifunctional) and thexyl hydroborane (difunctional) were used to attach PM branches on the backbone through hydroboration and polyhomologation. However, since intermolecular and intramolecular hydroboration reactions are possible, either cross-linked polymers or polymers with left-over double bonds will be formed. This problem could only be solved with a monofunctional hydroborane (Scheme S1, B).

Inspired by this monofunctional hydroborane strategy, new borate containing initiators leading to PM-based macromolecular architectures is under investigation. For example, alkene borates generated from hydroboration with alkyne are applied in polyhomologation (Scheme S1, C). The potential of this strategy is limited only by our imagination.

Synthesis of Initiator 2



2

The following procedure is the general procedure for the preparation of Allylpinacolboronate **2**: A 25 mL pre-dried flask equipped with a stirring bar was charged with magnesium turnings (0.08 g, 3.3 mmol) and fitted with a rubber septum. Under argon protection, dry THF was injected to the flask followed by PinBH (0.40 mL, 2.74 mmol). To the above mixture allyl bromide (0.23 mL, 2.74 mmol) was added dropwise with constant stirring over 10 minutes at room temperature. After 30 min of stirring at this temperature, another 1 equiv. of allyl bromide was added to the mixture. After two hours stirring at room temperature, the magnesium turnings were fully consumed. Then the mixture was diluted with hexane (10 mL) and quenched with aqueous 0.5 M HCl (10 mL) under 0 ^{o}C. After 15 mins of stirring the reaction mixture was transferred to a separatory funnel and extracted with hexanes (twice, 2x20 mL). The combined organic layers were dried over anhydrous Na_2SO_4, filtered and after chromatography (or distilled at room temperature under 1 Torr), a clear colorless oil was obtained in 85% yield (391 mg). Initiator **11** was synthesized follow the same procedure by using crotyl bromide instead of allyl bromide.

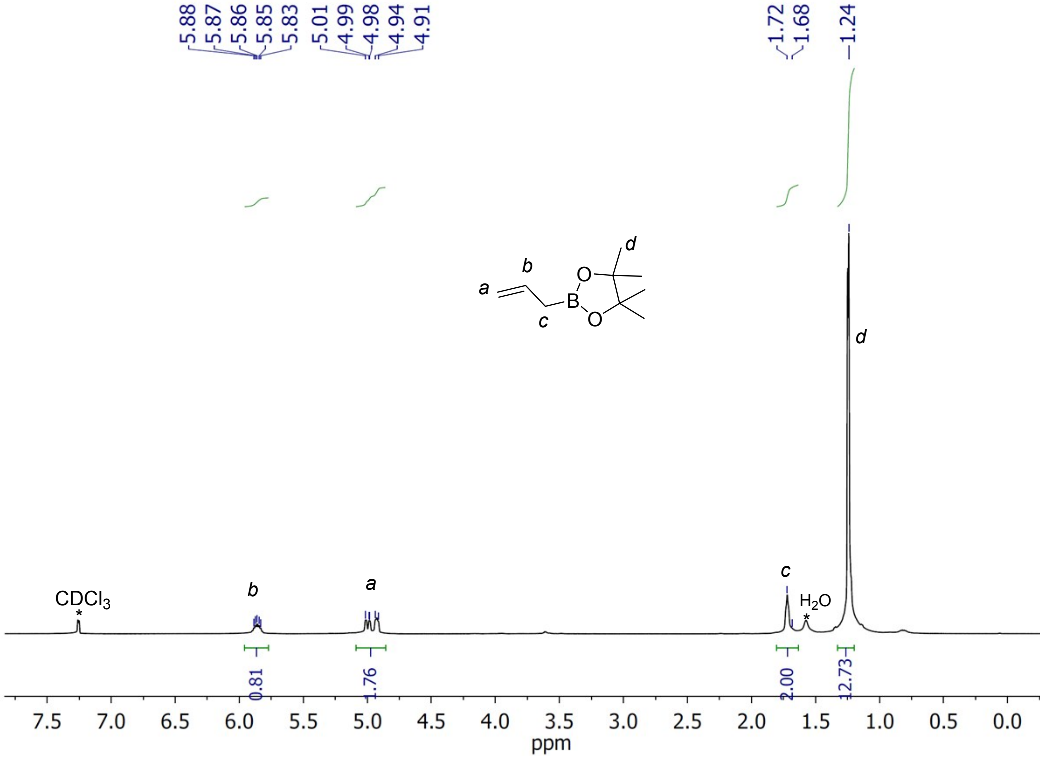


Figure S1 ^{1}H NMR spectrum of initiator **2** ($CDCl_3$, 25 °C, 600 MHz)

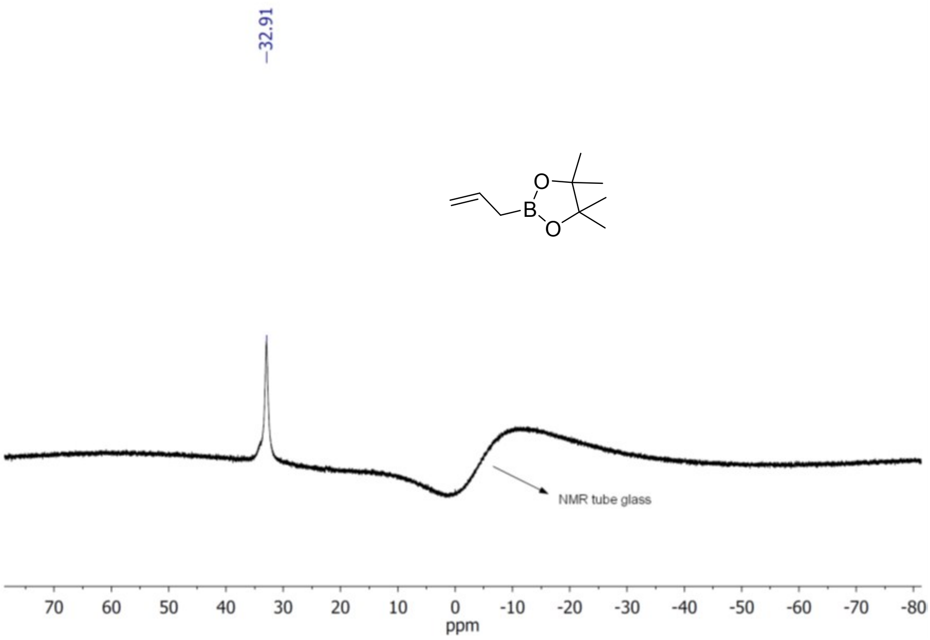


Figure S2 ^{11}B NMR spectrum of initiator **2** ($CDCl_3$, 25 °C, 600 MHz)

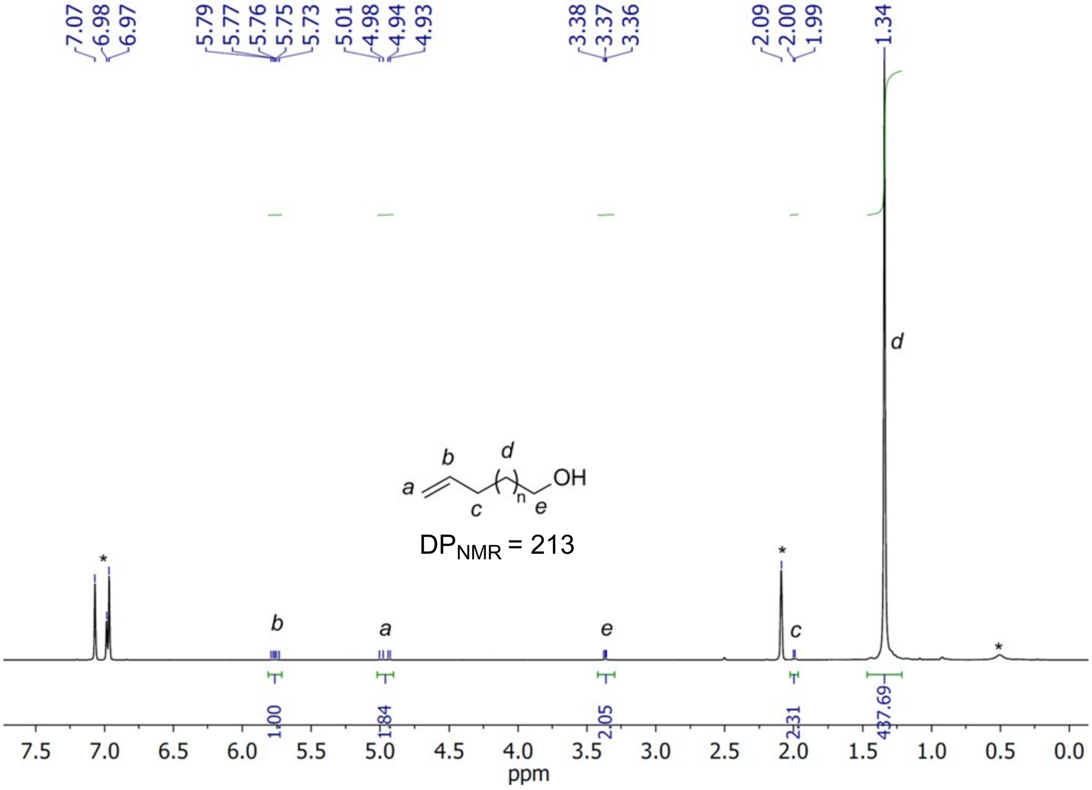


Figure S3 ^{1}H NMR spectrum of polymer **3** (full spectrum, d$_8$-toluene, 90 ^{o}C, 600 MHz, DP$_{NMR}$ =213 by NMR)

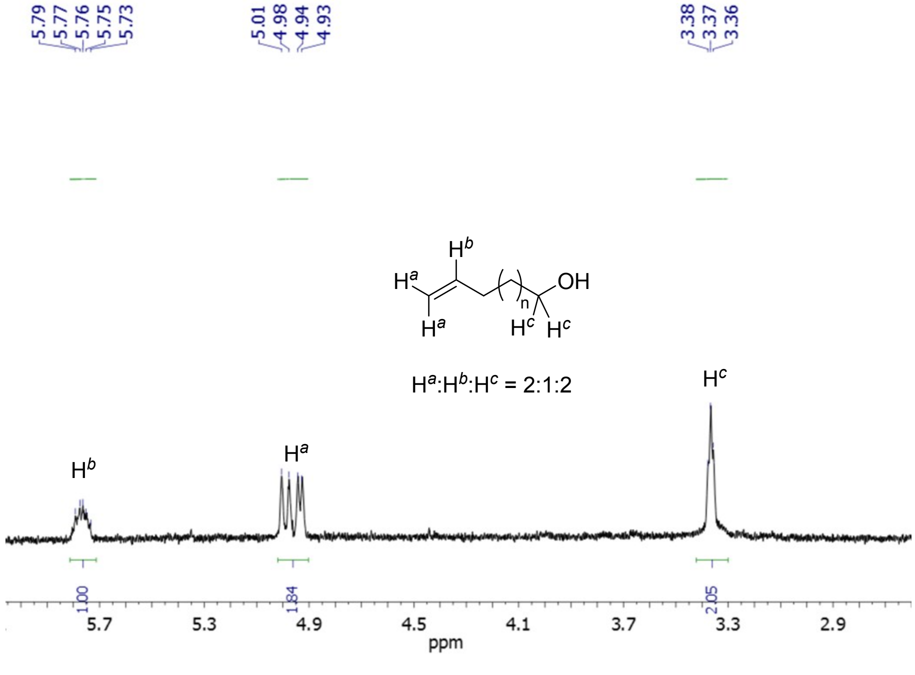


Figure S4 ^{1}H NMR spectrum of polymer **3** (partly enlarged, d$_8$-toluene, 90 ^{o}C, 600 MHz)

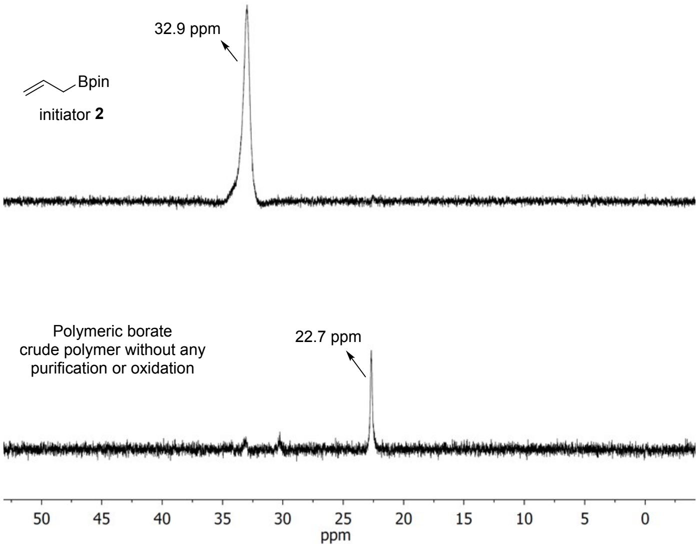
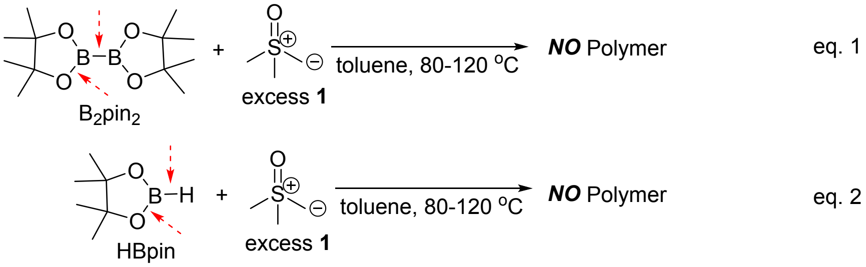


Figure S5 ^{11}B NMR spectra of crude polymer **3** before oxidation/hydrolysis compared with the initiator **2** (d_8-toluene, 25 ^{o}C, 600 MHz, baseline correction)



Scheme S2 Using B_2pin_2 or HBpin to initiate the polyhomologation of ylide monomer **1**

The polymerization of ylide **1** with B_2pin_2 doesn't give PM even at 120 ^{o}C. This can be attributed to the high stability of B-O and B-B bonds of B_2pin_2, having as consequence the blockage of the methylene insertion (ESI, Scheme S2, eq.1). Similarly, in the case of HBpin no polymer was produced, meaning that both B-H bond and B-O do not promote polyhomologation (ESI, Scheme S2, eq. 2). This is most likely due to the low initiation ability of HBpin or it react with strong basicity of sulfoxonium methylide **1** to generate unknown borate complex that not able to further initiation of polyhomologation.

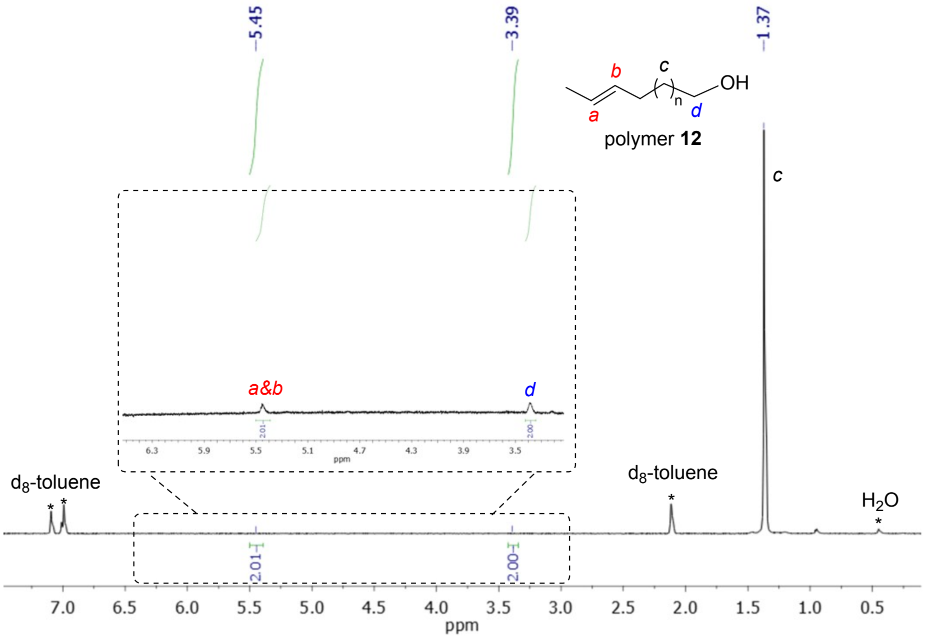
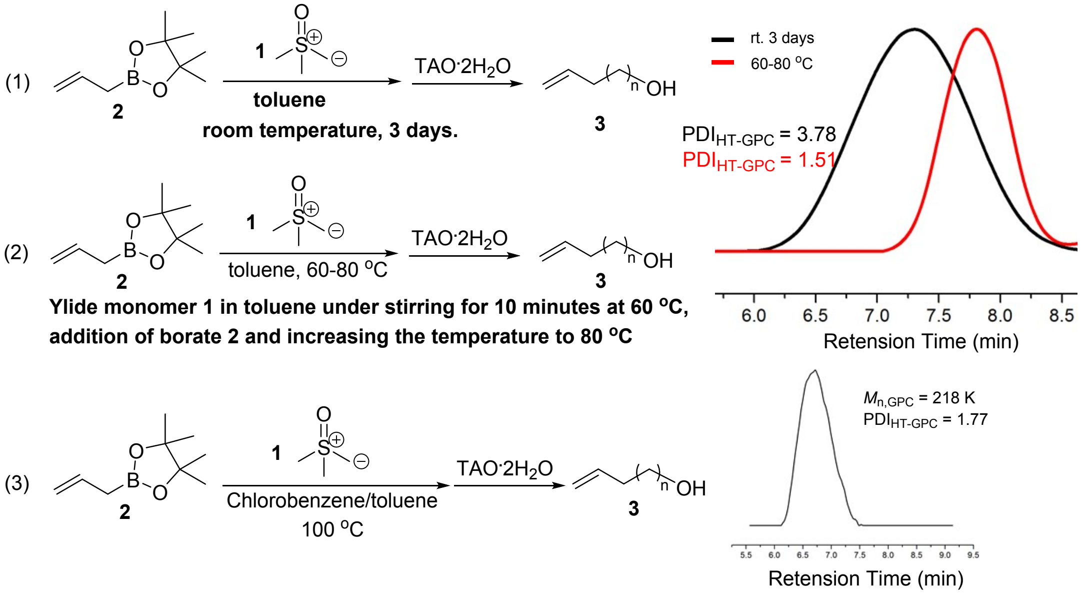


Figure S6 ^{1}H NMR spectrum of polymer **12** (d_8-toluene, 90 ^{o}C, 600 MHz)

Table S1 Influence of solvent and temperature on borate initiated polyhomologation

Entry^a	**DP$_{cal}$**^{b}	**DP$_{NMR}$**^{c}	**solvent**	**T (^{o}C)**	**Time(min)**	**PDI**^{d}
1	30	185	toluene	rt	-^{e}	3.78
2	30	166	toluene	60	40^f	1.51
3	30	-^{g}	Chlorobenzene/toluene	100	15	1.77
4	30	385	toluene	90	45^h	1.22

[a] All polymerization were carried out using allylic borate 1. [b] DP$_{cal}$ is the degree of polymerization, calculated from [M]/[I]. [c] DP$_{NMR}$ were determined by ^{1}H NMR (d_8-toluene, 90 ^{o}C, 600MHz). [d] PDI were determined versus polystyrene standards by high temperature GPC (TCB as solvent at 150 ^{o}C). [e] Stirring for 3 days. [f] Heating the mixture of initiator and monomer at 60 ^{o}C for 10 minutes and then increased the temperature to 80 ^{o}C for 30 minutes. [g] The chain-end groups were difficult to be detected because of high molecular weight. [h] The mixture of initiator and monomer stirring at room temperature for 30 minutes and then at 90 ^{o}C for 15 minutes.



Scheme S3 Borate **2** initiated polyhomologation at room temperature, 80 °C and 100 °C with corresponding HT-GPC traces (TCB, 150 °C)

The polymerization of ylide **1** (3.0 mmol) with **2** (0.1 mmol) at room temperature (DP_{cal} = 30) was incomplete even after 3 days. The reaction mixture was cloudy and a white solid precipitated by addition of the non-solvent ethanol (DP_{NMR} = 185, $PDI_{HT\text{-}GPC}$ = 3.78, ESI, Scheme S3, eq.1). Heating the mixture (monomer **1**, 3.0 mmol; allyl borate **2**, 0.1 mmol) in toluene at 60 °C for 10 minutes, then increasing the temperature to 80 °C the reaction mixture became neutral within 30 minutes (pH = 7.0), indicating the complete consumption of monomer **1**. After oxidation/hydrolysis, a polymer **3** with a relative narrow PDI but higher molecular weight than the calculated one was obtained (DP_{NMR} = 166, $PDI_{HT\text{-}GPC}$ = 1.51, ESI, Scheme S3, eq.2). We also observed that the reaction mixture turns cloudy in toluene at 80 °C, meaning that the high PDI maybe caused due to the poor solubility of the high molecular weight PM in toluene at 80 °C. To identify if the heterogeneity is the source of the higher than the calculated value of molecular weight and the broad molecular distribution, a mixture of chlorobenzene and toluene was used as solvent at 100 °C. The polyhomologation reaction proceeded smoothly and homogeneously, however the molecular weight and PDI were also uncontroled ($M_{n,HT\text{-}GPC}$ = 218 kg/mol, $PDI_{HT\text{-}GPC}$ = 1.77, ESI, Scheme S3, eq.3).

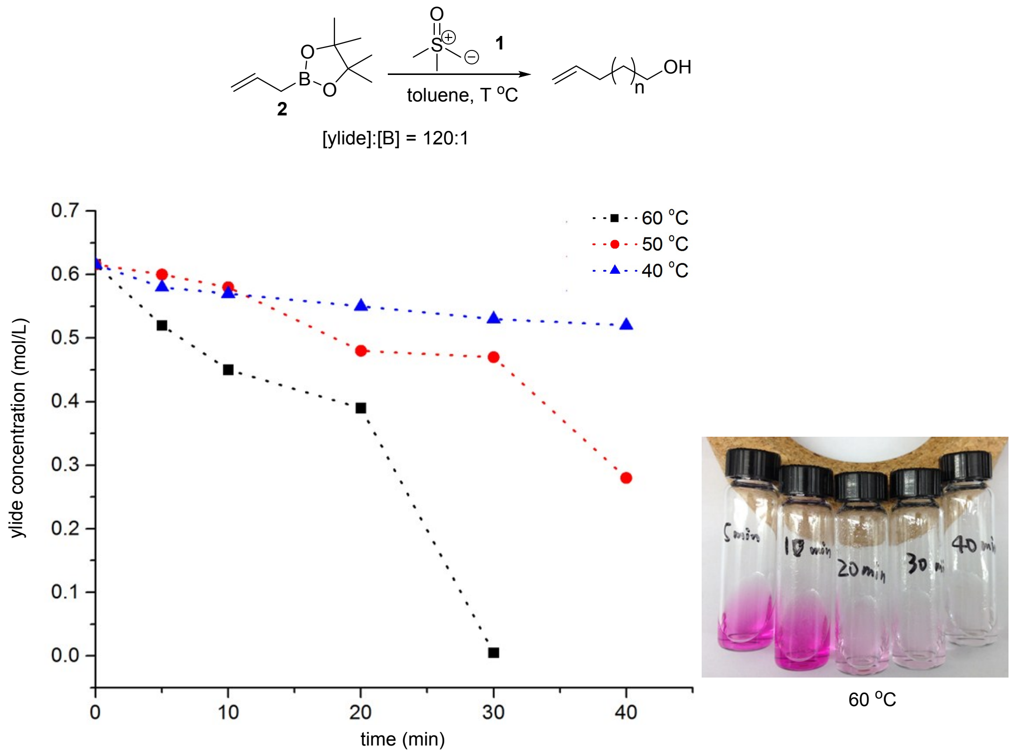
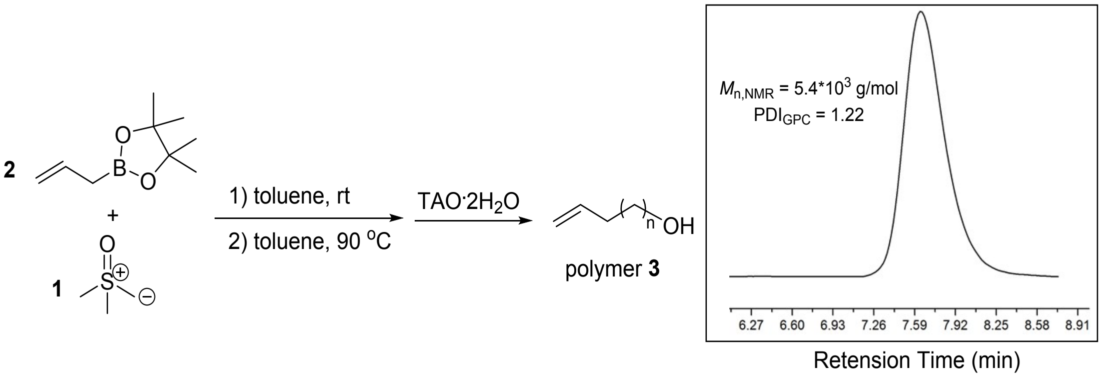


Figure S7 Influence of the temperature on the borate initiated polyhomologation of ylide monomer **1**



Scheme S4 Two-step polyhomologation reaction initiated by allylic borate

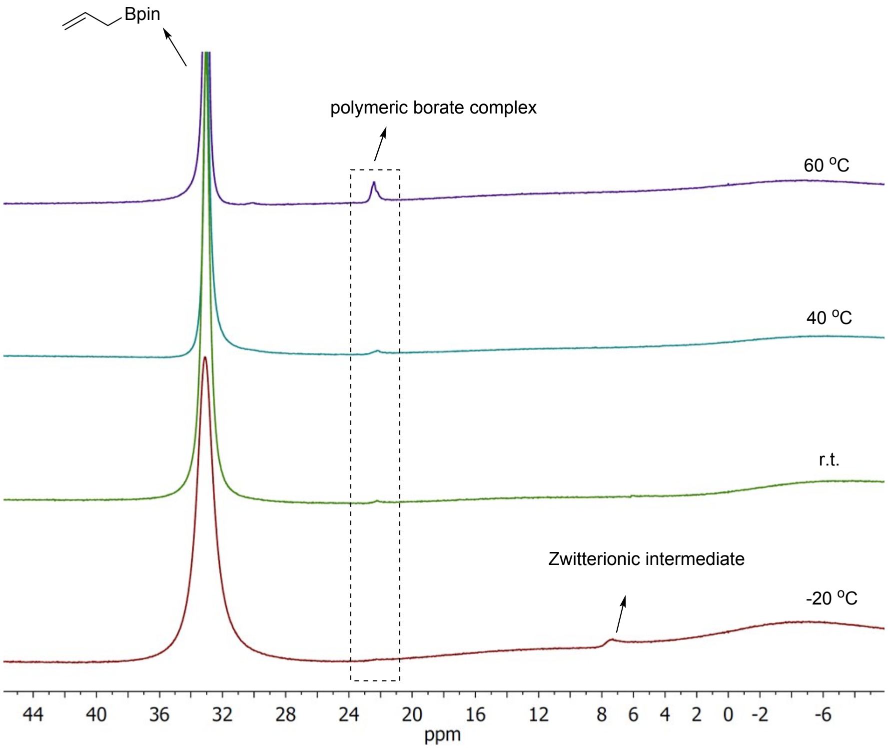


Figure S8 ^{11}B NMR spectra of initiator **2** with ylide monomer **1** ([I]/[M] = 1/1) at different temperatures (d_8-toluene, 600 MHz).

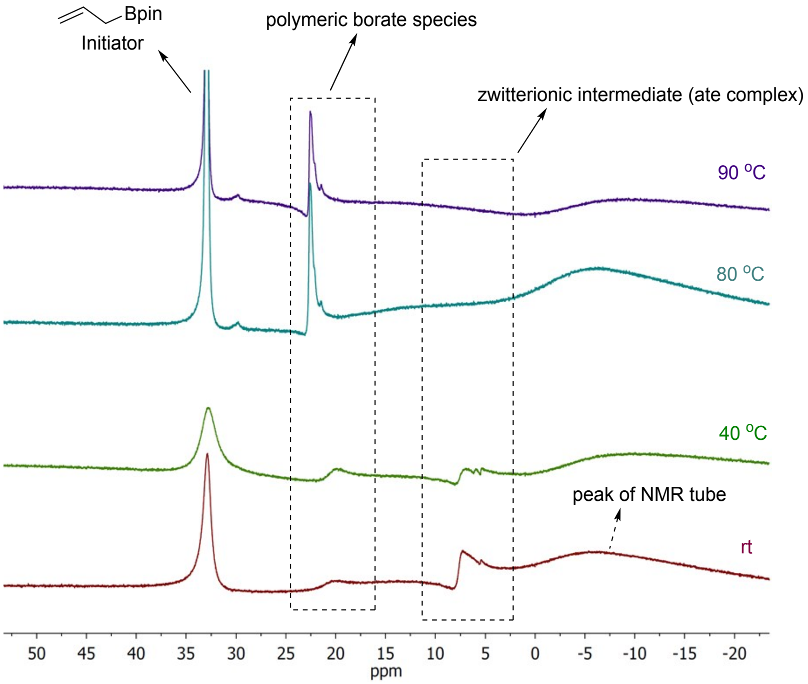


Figure S9 ^{11}B NMR spectra of initiator **2** with ylide monomer **1** ([I]/[M] = 1/10) at different temperatures (d_8-toluene, 600 MHz).

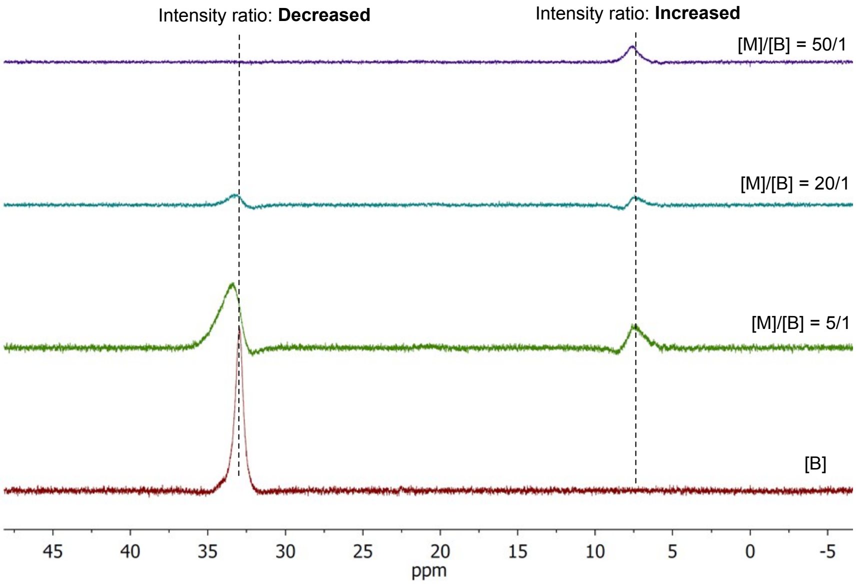
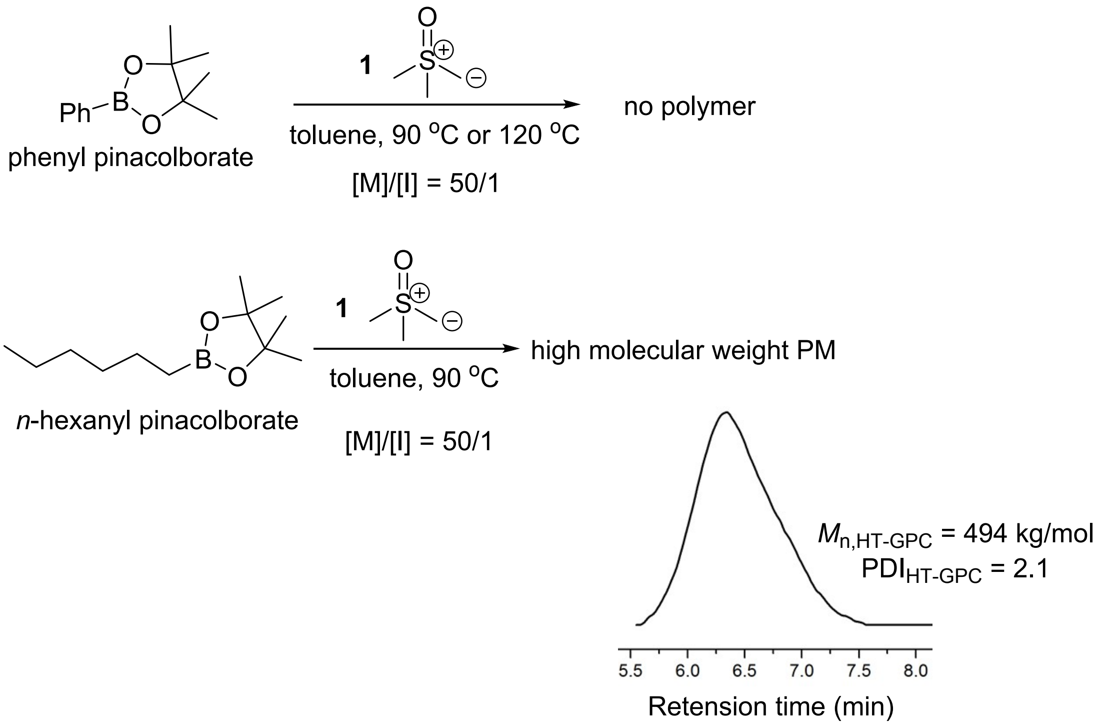


Figure S10 ^{11}B NMR spectra of ylide monomer with initiator at different concentrations ([M]/[B], C_6D_6, 25 ^{o}C, 600MHz, baseline correction)



Scheme S5 Substituted borates initiators for polyhomologation of ylide monomer **1**

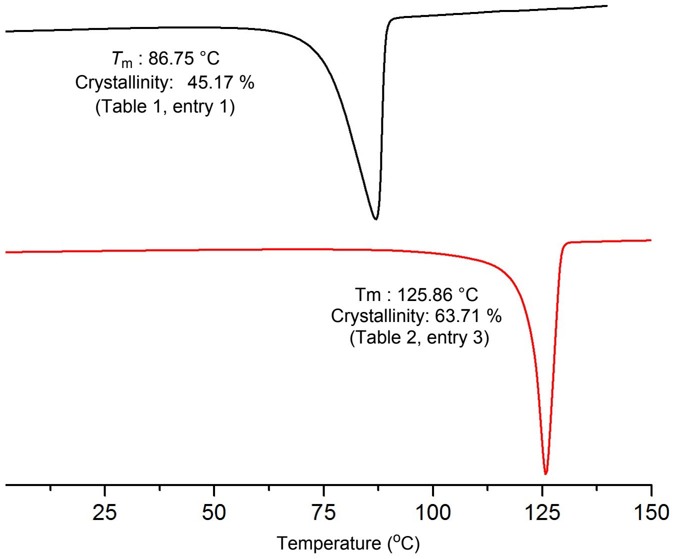


Figure S11 DSC thermographs of heterobifunctional polymer **3** (Table 1, entry 1 and 3). For low molecular weight (Table 1, entry 1, $M_{n,NMR}$ = 2.3 kg/mol) polymer **3**, melting temperature (T_m) is 86.75 ^{o}C with crystallinity 45.17%. WIncreasing the molecular weight (Table 1, entry 1, $M_{n,NMR}$ = 13.1 kg/mol), the melting temperature (T_m) increased 125.86 ^{o}C with crystallinity of 63.71%. These values of T_m are confirm the linear nature of the low molecular weight and high molecular weight polymers.

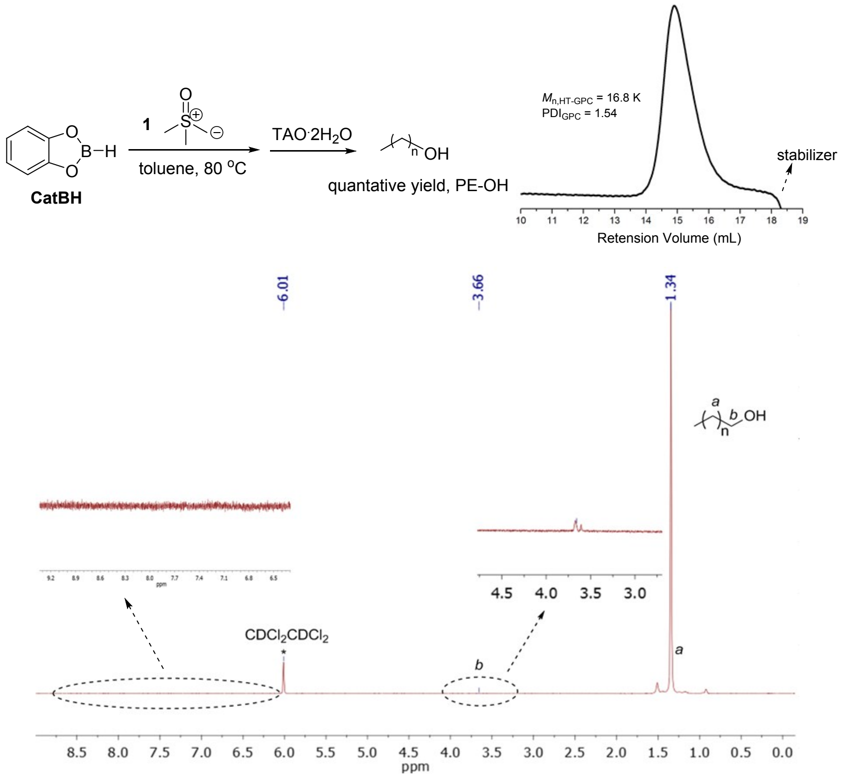
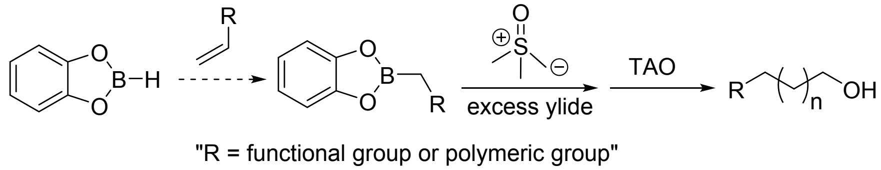


Figure S12 Catecholborane (CatBH) initiated polyhomologation of ylide monomer **1** in toluene at 80 ^{o}C

Initial experiments using catecholborane (CatBH) to initiate polyhomologation of dimethylsulfoxonium methylide **1** in toluene at 80 °C, were successful (all ylide monomer consumed within 15 min, $M_{n,\text{HT-GPC}}$ = 16.8 kg/mol, PDI_{GPC} = 1.54). In the ^{1}H NMR spectrum of the polymer the fingerprint of aryl protons are absent, meaning that B-O bonds are inactive (ESI, Figure S11).



Scheme S6 Proposed work on catecholborane (CatBR) initiated polyhomologation of ylide monomer

Reference:

[1] J. W. Clary, T. J. Rettenmaier, R. Snelling, W. Brykes, J. Banwell, W. T. Wipke, B. Singaram, *J. Org. Chem.,* 2011*,* ***76****,* 9602-9610.