

## Boron-Mediated Polymerization of Ylides Derived from Allylic Arsonium Salts: Influence of the Double Bond Substitution on the Outcome

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### Supporting information

**General:** THF was freshly distilled from sodium benzophenone ketyl. Reactions were performed under an argon atmosphere. TLC: Silica Gel 60F<sub>254</sub> plates (Merck), with detection by UV light and by an ethanol solution of phosphomolybdic acid. Column chromatography: 40-63  $\mu\text{m}$  Merck Silica Gel. NMR: Bruker AM 300 (300.13 and 75.47 MHz for <sup>1</sup>H and <sup>13</sup>C, respectively). CDCl<sub>3</sub> was used as solvent; chemical shifts ( $\delta$ ) are in ppm (s = singlet, d = doublet, t = triplet, m = multiplet, b = broad); coupling constants ( $J$ ) are in Hz.

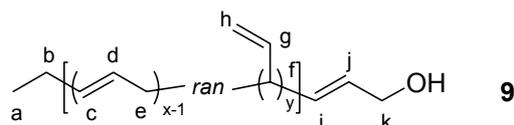
**Size exclusion chromatography procedure.** Number average molecular weights ( $M_n$ ), weight average molecular weights ( $M_w$ ), and molecular weight distributions ( $M_w/M_n$ ) were determined using steric exclusion chromatography (SEC) according to two procedures.

Procedure A (used except when noted): Elution in THF at 30°C with a flow rate of 1 mL.min<sup>-1</sup>. Two 7.5 mm diameter  $\times$  300 mm Polymer Labs 3  $\mu\text{m}$  particle diameter mixed-E PLgel columns were connected in line to a Shimadzu LC-10AD pump, a degasser (Erma, ERC-3312), a Shimadzu RID-6A differential refractive index (DRI) detector and a PD 2000 (Precision Detectors, Inc.) two-angle light scattering (TALLS) detector. The static measurements were done both at 15 degrees and 90 degrees, and simultaneously coupled to a Dynamic Light Scattering analysis. The reported values of  $M_n$  and  $M_w$  were obtained from the measurements at 90 degrees.

Procedure B: Elution in THF at 25°C with a flow rate of 1 mL.min<sup>-1</sup>. Two 7.5 mm diameter  $\times$  300 mm Polymer Labs 10  $\mu\text{m}$  particle size PLgel columns, were connected in line to a Knauer differential refractometer. The reported values of  $M_n$  and  $M_w$  were determined versus polystyrene standards.

### Typical preparation of polymer 9.

**Polymer 9** (initial ylide/Et<sub>3</sub>B ratio = 15; see table 1, entry 1). To a suspension of allyltriphenylarsonium tetrafluoroborate (0.469 g, 1.08 mmol) in anhydrous THF (10 mL) cooled to -78°C, was added dropwise a 1.7 M solution of *tert*-butyllithium in pentane (0.637 mL, 1.08 mmol). Stirring was continued for 40 min at -78°C, then 5 min at 0°C. To the bright red solution obtained was added at once a 1 M solution of triethylborane in hexane (72  $\mu\text{L}$ , 0.072 mmol). An instantaneous discoloration of the solution occurred. The pale yellow solution was stirred for 1 h at 0°C, and then a previously combined mixture of 30% hydrogen peroxide (5 mL) and of 15% sodium hydroxide was added cautiously. The reaction mixture was then vigorously stirred for one night at room temperature. An aqueous saturated NH<sub>4</sub>Cl solution (40 mL) was added. The aqueous phase was extracted with dichloromethane (3  $\times$  15 mL). The combined organic phases were dried over MgSO<sub>4</sub> then concentrated under vacuum. Silica gel chromatography (pentane, then 6:4 pentane/AcOEt) afforded polymer 9 as a pale yellow oil (44.4 mg, 84 %). Degree of polymerization according to the NMR spectrum: 7.7; according to SEC: 5.8.



**Polymer 9** (table 1, entry 1).  $^1\text{H}$  NMR ( $\text{CDCl}_3$ , 300 MHz):  $\delta$  = 5.81-5.57 (m, 4.0H, Hg,i,j), 5.50-5.32 (m, 8.5H, Hc,d), 5.05-5.00 (m, 4.9H, Hh), 4.12 (d,  $J$  = 4.9 Hz, 2H, Hk), 2.77-2.52 (m, 7.6H, bis(allylic) He, bis(allylic) Hf), 2.08-1.96 (m, 5.1H, allylic He, Hb  $\alpha$  to internal double bond), 1.45-1.27 (m, 3.4H, Hb  $\alpha$  to propenylidene), 0.98 (td,  $J_1$  = 7.3 Hz,  $J_2$  = 3.1 Hz, 2.1H, Ha  $\beta$  to internal double bond), 0.88 (t,  $J$  = 7.3 Hz, 1.5H, Ha  $\beta$  to propenylidene). Size exclusion chromatography:  $M_w$  = 316,  $M_n$  = 277, PDI = 1.14.

**Polymer 9** (table 1, entry 2). Size exclusion chromatography:  $M_w$  = 679,  $M_n$  = 620, PDI = 1.10.

**Polymer 9** (table 1, entry 3):  $^{13}\text{C}$  NMR ( $\text{CDCl}_3$ , 75 MHz):  $\delta$  = 141.5 (Cg), 133.9-131.5 (Ci,j and Cc,d if Ce is allylic), 130.1-128.4 (Cc,d if Ce is bis(allylic)), 115.6-114.0 (Ch), 63.7 (Ck), 48.5-46.8 (Cf), 38.2 (allylic Ce), 35.7 and 35.2 (bis(allylic) Ce). Size exclusion chromatography:  $M_w$  = 948,  $M_n$  = 871, PDI = 1.09.

Assignments of NMR signals for polymer **9** were made on the basis of  $^1\text{H} / ^1\text{H}$  COSY 90 (Figure 1) and  $^1\text{H} / ^{13}\text{C}$  HETCORR experiments.

### Supplementary experiments

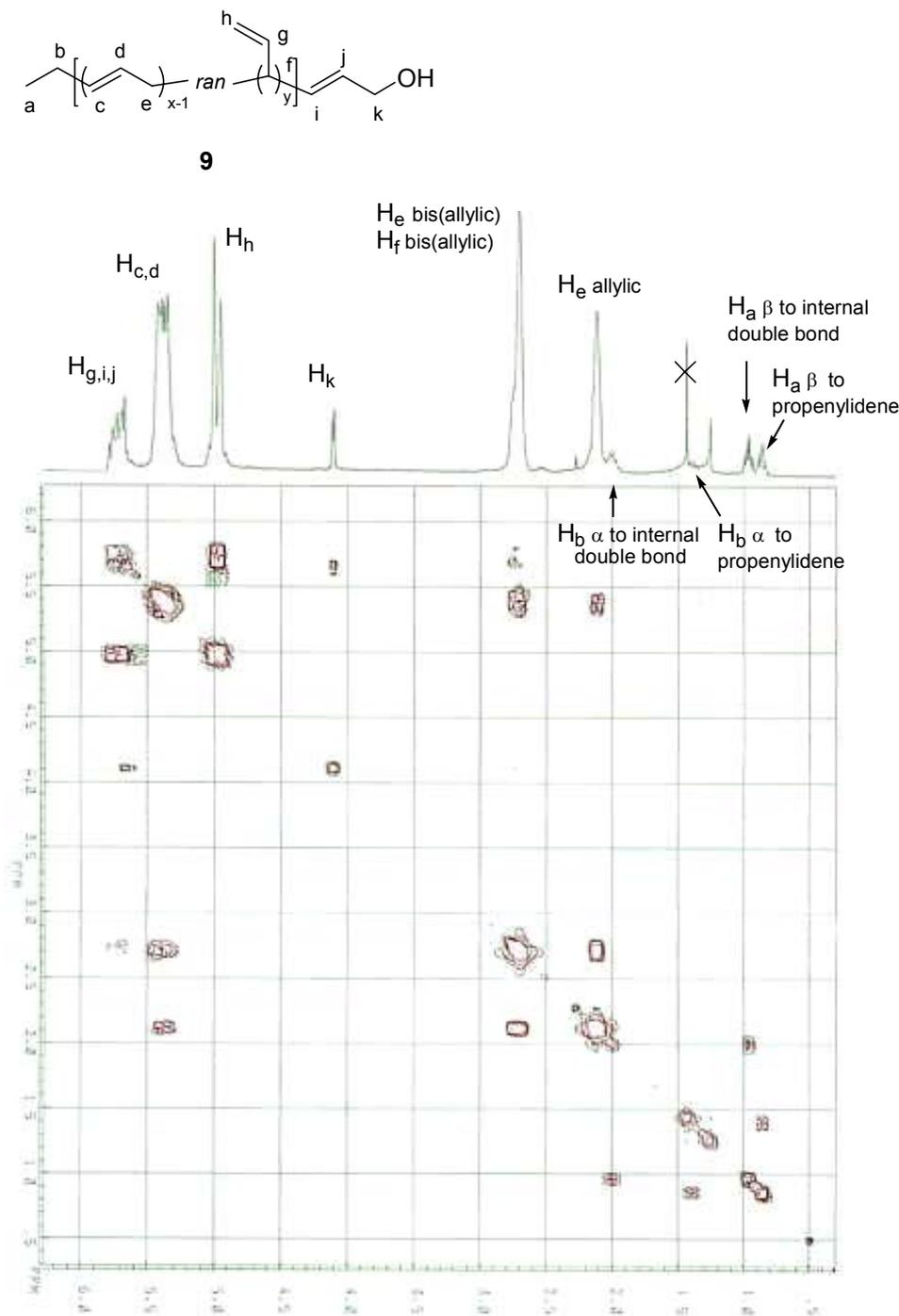
The possibility to increase the  $x / y$  ratio by performing the polymerization at different temperatures was evaluated. The reactions were carried out using tributylborane, with an initial molar ratio of ylide to organoborane,  $n = 9$  (Table).

**Table 1.** Effect of the temperature on the rearrangement ratio in polymer **9'**

Entry	$T$ ( $^\circ\text{C}$ )	$x / y$ ratio	$\text{DP}_{\text{RMN}}$	Yield (%)
1	-78	1.5 / 1	3.3	34
2	-20	1.8 / 1	3.6	31
3	0	3.2 / 1	3.4	41
4	0 <sup>a</sup>	8.6 / 1	7.2	68

<sup>a</sup>The ylide solution was added dropwise to the tributylborane in THF.

It was observed that the proportion of double bond incorporated in the polymer main chain increased as the temperature at which the organoborane was added increased (entries 1-3). However, there was still an important proportion of vinyl groups in the best case. A notable improvement of the  $x / y$  ratio was obtained by adding the ylide dropwise to the tributylborane solution at 0  $^\circ\text{C}$  (entry 4). Interestingly, under these conditions, the degree of polymerization was significantly higher.



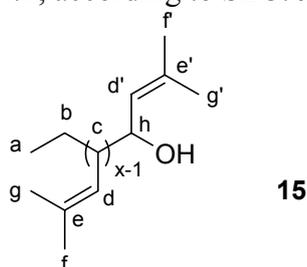
**Figure 1.**  $^1\text{H}/^1\text{H}$  COSY 90 experiment, polymer **9**.

Interestingly, it was observed that polymer **9** is a primary alcohol. This is not unexpected, since at the end of the polymerization process, the reaction of the allylic boranes with the ylide cannot compete with the rearrangement anymore. The less crowded polymeric organoborane, in which the boron atom is bonded to three methylene groups, is then formed, and after oxidation, a primary alcohol is obtained.

Moreover, two vinyl groups are never bonded to two consecutive chain carbon atoms. This presumably indicates that the presence of two consecutive pendant groups induces an important steric crowding, thus favoring the [1,3] sigmatropic rearrangement.

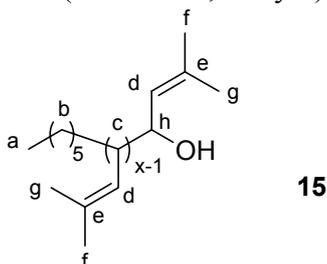
### Typical preparations of polymer **15**.

Polymer **15** (R = Et, see table 2, entry 3) from diethylmethoxyborane (initial ylide/Et<sub>2</sub>BOMe ratio = 9). To a suspension of prenyltriphenylarsonium tetrafluoroborate (0.383 g, 0.829 mmol) in anhydrous THF (10 mL) cooled to -40°C, was added dropwise a 1.7 M solution of *tert*-butyllithium in pentane (0.463 mL, 0.788 mmol). Stirring was continued for 40 min at -40°C. To the blood-red solution obtained was added at once a 1 M solution of diethylmethoxyborane in THF (88 μL, 0.088 mmol). Stirring was continued at -40°C. The discoloration of the reaction mixture occurred over 4 h. To the pale yellow solution obtained was then added cautiously a previously combined mixture of 30% hydrogen peroxide (5 mL) and of 15% sodium hydroxide. The reaction mixture was then vigorously stirred for 4h. An aqueous saturated NH<sub>4</sub>Cl solution (40 mL) was added. The aqueous phase was extracted with dichloromethane (3 x 15 mL). The combined organic phases were dried over MgSO<sub>4</sub> then concentrated under vacuum. Silica gel chromatography (pentane, then 4:6 pentane/AcOEt) afforded polymer **15** as a viscous, colorless oil (33.0 mg, 53 %). Degree of polymerization according to the NMR spectrum: 14.1; according to SEC: 9.7.



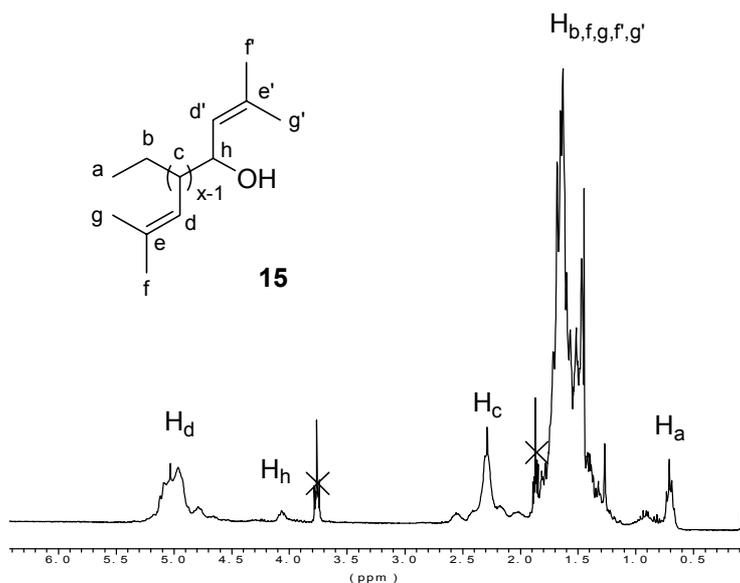
**Polymer 15** (R = Et, table 2, entry 3). <sup>1</sup>H NMR (CDCl<sub>3</sub>, 300 MHz): δ = 5.11-4.79 (m, 14.2H, Hd,d'), 4.07 (m, 1H, Hh), 2.56-2.01 (m, 10.3H, Hc), 1.82-1.27 (m, 92.7H, Hb,f,g,f',g'), 0.93-0.69 (m, 5.5H, Ha). <sup>13</sup>C NMR (CDCl<sub>3</sub>, 75 MHz): δ = 130.2-129.6 (Ce,e'), 126.5-122.8 (Cd,d'), 71.3 (Cc'), 44.8-42.6, 30.2 (Cc), 29.6 (Cb), 26.4-25.9 (Cf,f'), 18.7-18.2 (Cg,g'), 12.3 (Ca). Size exclusion chromatography: Mw = 860, Mn = 705, PDI = 1.22.

Polymer **15** (R = hexyl, table 2, entry 4) from hexyl-1,3,2-dioxaborinane (initial ylide/boronate ratio = 10). To a suspension of prenyltriphenylarsonium tetrafluoroborate (2.02 g, 4.37 mmol) in anhydrous THF (40 mL) cooled to -40°C, was added dropwise a 2.5 M solution of *n*-butyllithium in hexane (1.75 mL, 0.788 mmol). Stirring was continued for 30 min at -40°C, leading to a blood-red solution. The temperature was raised to -20°C, then a solution of hexyl-1,3,2-dioxaborinane (74 mg, 0.437 mmol) in THF (1 mL) was added. Stirring was continued at -20°C for 3 h, and at room temperature for 10 h. To the colorless solution obtained was then added cautiously a previously combined mixture of 30% hydrogen peroxide (4 mL) and of 3N sodium hydroxide (4 mL). The reaction mixture was then vigorously stirred for 6 h. A solid which had precipitated was recovered by filtration, washed with methanol (3 x 10 mL) and dried under vacuum (white solid, 72 mg, 21%). Degree of polymerization according to SEC: 306 (see table 2, entry 4).

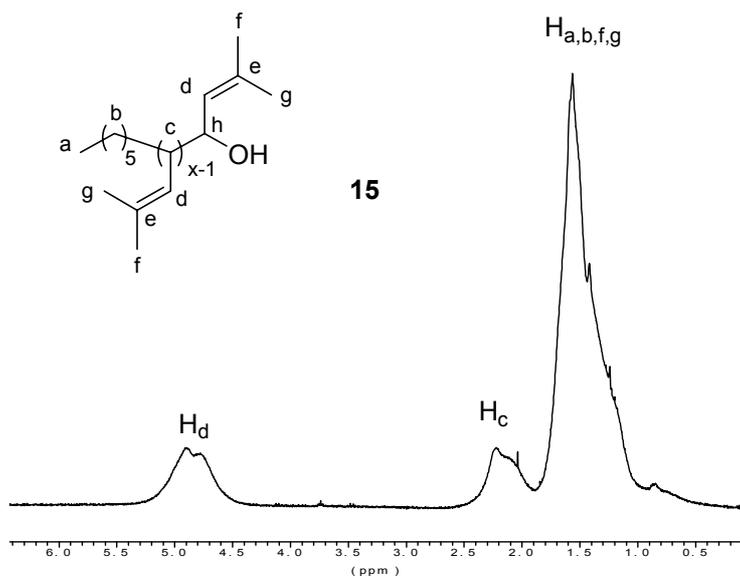


**Polymer 15** (R = hexyl, table 2, entry 4).  $^1\text{H}$  NMR ( $\text{CDCl}_3$ , 300 MHz):  $\delta = 5.35\text{-}4.38$  (br m,  $\text{H}_d$ ),  $2.57\text{-}1.89$  (br m,  $\text{H}_c$ ),  $1.88\text{-}0.69$  (br m,  $\text{H}_a, \text{b}, \text{f}, \text{g}$ ).  $^{13}\text{C}$  NMR ( $\text{CDCl}_3$ , 75 MHz):  $\delta = 131.0\text{-}123.2$  (Cd,e),  $46.3\text{-}40.9$  (Cc),  $26.7$  (Cf),  $20.5\text{-}16.8$  (Cg). Size exclusion chromatography (procedure B):  $M_w = 32650$ ,  $M_n = 20950$ ,  $\text{PDI} = 1.56$ .

Assignments of NMR signals for polymer **15** were also made on the basis of DEPT 135, DEPT 90 experiments.



**Figure 2.**  $^1\text{H}$  NMR spectrum of polymer **15** (table 2, entry 3).



**Figure 3.**  $^1\text{H}$  NMR spectrum of polymer **15** (table 2, entry 4).

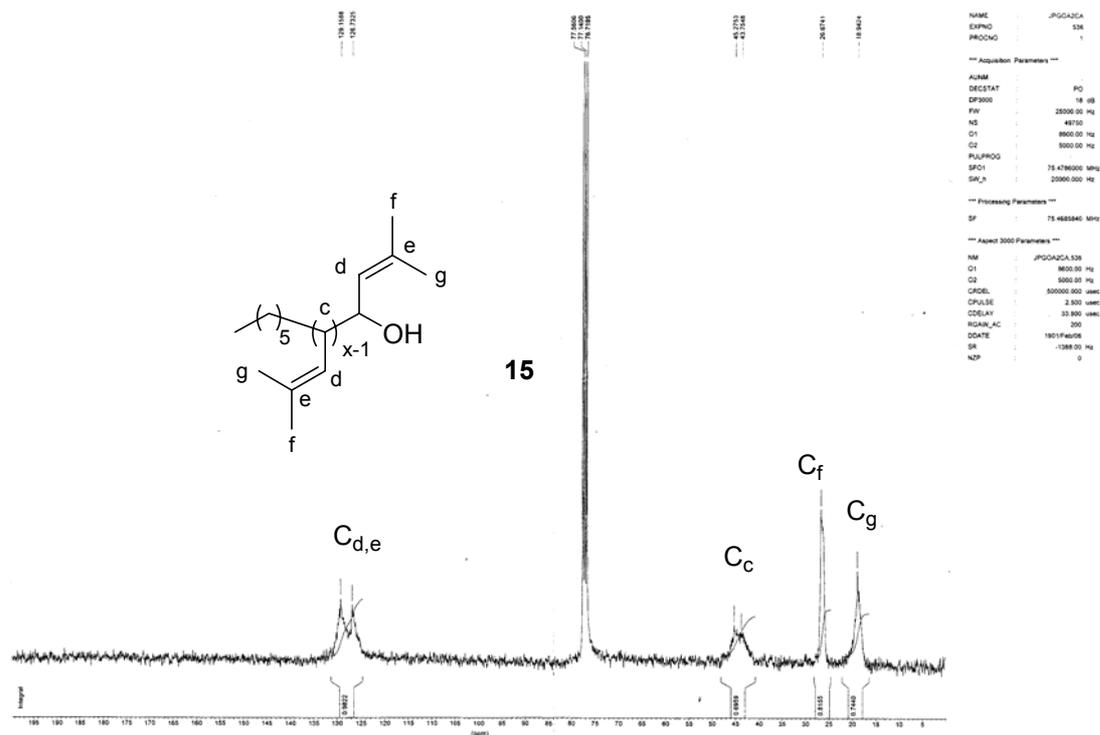


Figure 4.  $^{13}\text{C}$  NMR spectrum of polymer **15** (table 2, entry 4).

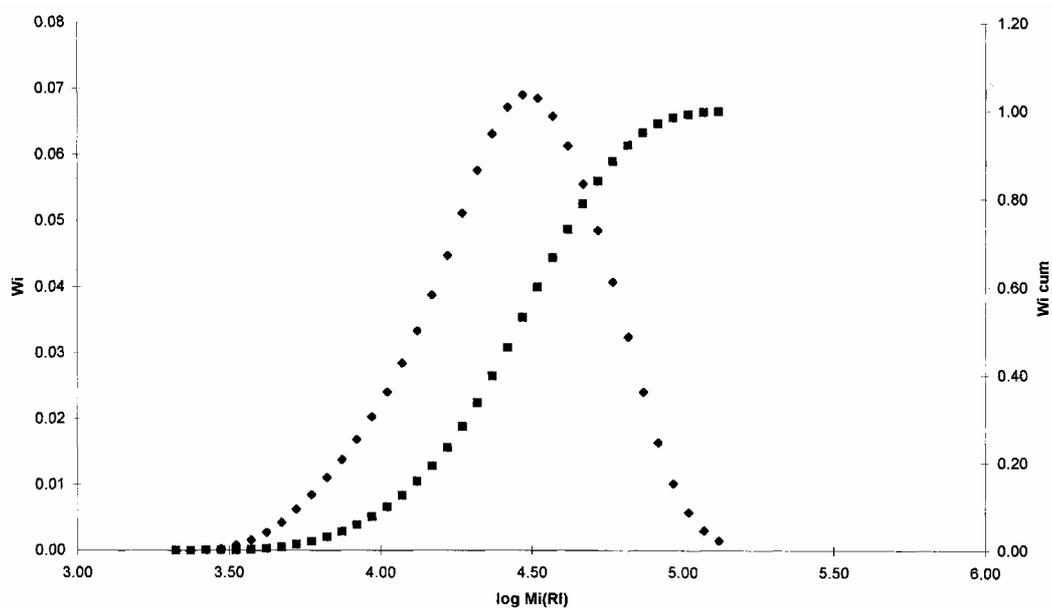


Figure 5. Size exclusion chromatogram of polymer **15** (table 2, entry 4).