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Synthesis of novel organoboron polymers by haloboration polymerization of bisallene compounds and their reactions

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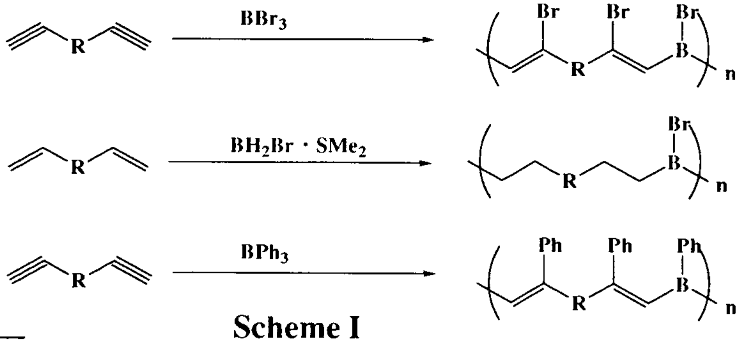
Summary

Novel organoboron polymers were prepared by haloboration polymerizatrion of bisallene compounds. The polymers obtained have allylborane halide units in their main chain and can be expected as a novel type of reactive polymers. For example, the polymer prepared by haloboration polymerization between tribromoborane (**1**) and 1,2,10,11-dodecatetraene (**2b**) was subjected to chain transformation reaction (dichloromethyl methyl ether rearrangement) to give the corresponding polyalcohol or polyketone. Haloboration-phenylboration polymerization of aliphatic bisallenes by using diphenylbromoborane also gave the corresponding polymers.

Introduction

Organoboron halides are very important reagents in organic synthesis, for ether cleavage [1], haloboration reaction [2] and so on. Therefore their polymeric materials are expected to be highly reactive polymers having unique properties. Recently, we have reported novel methodologies for the synthesis of poly(organoboron halide)s by using haloboration reaction, that is addition of B-X (X=Cl, Br) bond to terminal triple bond. Reactions between tribromoborane and various kinds of terminal diynes gave the corresponding poly(organoboron halide)s in good yields [3]. The polymers obtained can be regarded as polymeric Lewis acid which has scarcely ever been known. Furthermore, we reported another method for the preparation of poly(organoboron halide)s. Hydroboration polymerization of dienes with monobromoborane dimethylsulfide complex gave the corresponding polymers [4]. The obtained polymers were successfully converted to polyalcohols, polyketones or poly(diene)s by chain transformation reactions. Very recently, it was found that phenylboration reaction [5] (addition of B-Ph bond to terminal triple bond) can also be used for polymerization [6]. In this case, the polymer obtained showed high air-stability.



Scheme I

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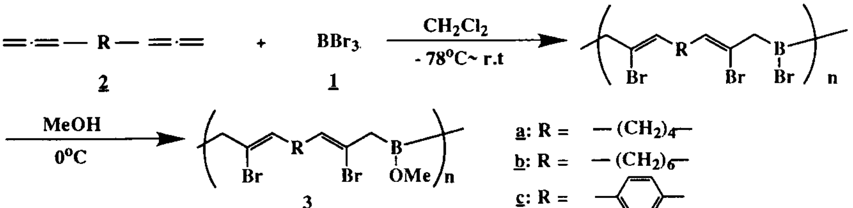
In this paper, synthesis of novel organoboron polymers by haloboration polymerization of bisallene compounds is described. The obtained polymers have allylboron halide units in their main chain and can be expected as a novel type of reactive polymers. Haloboration-phenylboration polymerization of aliphatic bisallenes by using diphenylbromoborane was also examined to give the corresponding polymers.

Results and Discussion

According to the previous report by Lappert et al. 7), the reaction of allenes with tribromoborane gives mainly haloboration adducts, similarly to acetylenes.

This reaction has been used for the preparation of allyl alcohols in organic synthesis 8). However, the direct application of this reaction to polymer synthesis has not ever been reported. As a typical example, haloboration polymerization between tribromoborane (1) and 1,2,10,11-dodecatetraene (2b) was examined here (Scheme II).



Scheme II

To a 1.0 M dichloromethane solution of 1, 2b was added at -78°C and then the reaction mixture was gradually warmed up to room temperature. The reaction mixture was subjected to GPC measurement and the polymerization was observed. However in the present polymerization, the polymer obtained was very unstable and evaporation of solvent gave only insoluble gel presumably due to the reaction with a trace amount of water. But after the treatment with methanol and substituting B-Br to B-OMe, it became stable for handling. After reprecipitation into methanol, a white gum was obtained. The polymer was soluble in common organic solvents such as THF, benzene and chloroform. The number-average molecular weight of this polymer was estimated to be 5000 from the result of GPC based on polystyrene calibration curves.

The structure of the polymer was supported by ^{1}H-, ^{11}B-NMR spectra and also by oxidative decomposition. ^{11}B-NMR spectrum of 3b is represented in Figure I. This spectrum has main peak at 27.8 ppm corresponding to diallylboron methoxide. Small peak at 18.5 ppm is assignable to the end group, allylboron dimethoxide. The molecular weight of the polymer increased when the feed ratio of two monomers approached to unity. This result indicates that the present polymerization proceeds in a polyaddition manner.

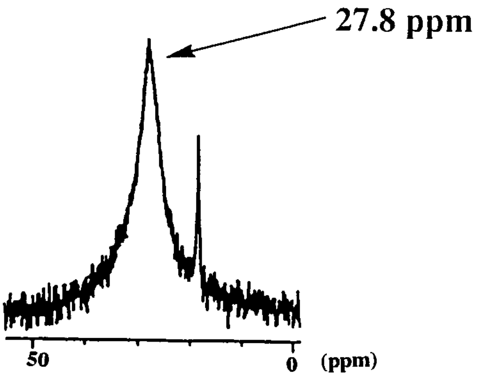


Figure I. ^{11}B-NMR spectrum of 3b

The results of polymerization between 1 and various bisallenes are listed in Table I. When 1,2,8,9-decatetraene (2a) and diallenylbenzene (2c) were used as allene monomers, the corresponding polymers were also obtained. But similarly with the case of hydroboration polymerization 9), the molecular weights of polymers prepared from 2a and 2c were relatively lower than that prepared from 2b. This might be explained by the same reason, that is some isomerization of bisallene during the polymerization due to lower stability of these monomers compared with **2b**.

Table I. Haloboration Polymerization of Various Bisallenes [a]

run	bisallenes (2)		1/2	Mw [b]	Mn [b]	yield (%) [c]
1	$=\cdot=-(CH_2)_4-=\cdot=$	(2a)	1.15	2600	1700	53
2	$=\cdot=-(CH_2)_6-=\cdot=$	(2b)	1.23	12000	5000	77
3		(2c)	1.17	8500	2300	71

a) Reactions were carried out in CH_2Cl_2 at -78°C, and then warmed up to r.t. b) GPC (THF), polystyrene standards. After the treatment with MeOH. c) Isolated yields after reprecipitation into MeOH.

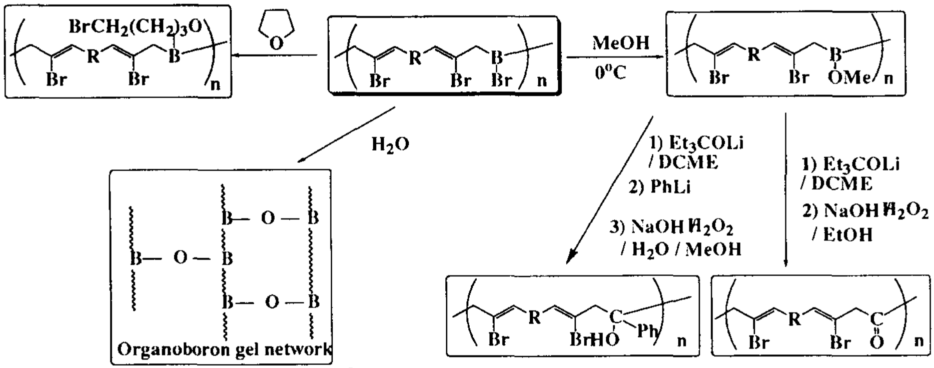
As boron monomers, trichloroborane and phenyldichloroborane were also examined for haloboration polymerization of **2b** (Table II). When trichloroborane was used, polydispersity of the obtained polymer was considerably wide (run 3) and a gelation was observed after longer reaction time (run 4). This result shows that haloboration polymerization of **2b** with trichloroborane is not desirable because of the difficulty in control of polymerization. A bifunctional monomer, phenyldichloroborane was also employed for the polymerization and the results are shown in runs 5-7. Similarly to the case of runs 3-4, wide polydispersity was observed when the reaction time became longer (run 7). This indicates that phenylboration reaction also took place after long reaction time and phenyldichloroborane does not necessarily work as a bifunctional monomer, even under mild reaction condition (room temperature).

Table II. Haloboration Polymerization of Bisallene (2b) with Various Borane Reagents [a]

Run	Borane Reagent	Borane / 2b (ratio)	Temp (°C)	Time (h)	Mw [b]	Mn [b]	Mw / Mn [b]	yields (%) [c]
1	BBr_3	1.21	0 - r.t.	12	2800	2200	1.3	31
2	BBr_3	1.23	-78 - r.t.	12	12000	5000	2.4	77
3	BCl_3	1.05	0 - r.t.	12	36000	8700	4.1	72
4	BCl_3	1.04	0 - r.t.	24	-	-	-	- [d]
5	$PhBCl_2$	1.20	0 - r.t.	12	2300	1300	1.8	83
6	$PhBCl_2$	1.24	0 - r.t.	24	7600	2700	2.8	68
7	$PhBCl_2$	1.10	0 - r.t.	48	30000	6000	5.0	82

a) Reactions were carried out in CH_2Cl_2. b) GPC (THF), polystyrene standards. After the treatment with MeOH. c) Isolated yields after reprecipitation into MeOH. d) Gelation was observed.

The polymers prepared by haloboration polymerization of bisallenes have allylboron halide units in their main chain. Therefore, they are expected to have different reactivity compared with polymers prepared from diynes having alkenylboron halide units. Various polymer reactions were performed in polymer **3b** (Scheme III). Generally, boron halides are widely used for ether cleavage as Lewis acid. Taking advantage of the property, ring-opening reaction of THF was carried out. To the poly(organoboron halide) prepared from **1** and **2b**, THF was added at 0°C and the reaction mixture was gradually warmed up to room temperature. Evaporation of solvent gave the corresponding polymer having 4-bromobutoxy group in their side chain quantitatively. Then the polymer **3b** was subjected to chain transformation reaction (DCME rearrangement). To a THF solution of **3b**, 3-ethyl-3-pentanol lithium alkoxide and DCME were added at 0°C and the reaction mixture was stirred for 2h at room temperature. The solvent was evaporated and the residue was dissolved in benzene. Phenyllithium in cyclohexane was added at -78°C and then the reaction mixture was stirred for 12h. After oxidative treatment with $NaOH/H_2O_2/H_2O/MeOH$ at 60°C for 2h, extraction and evaporation of the solvent gave the corresponding polyalcohol (Mn 2400, yield 68%). When the reaction mixture of DCME rearrangement was directly oxidated, the corresponding polyketone was obtained (Mn 900, yield 51%).



Scheme III

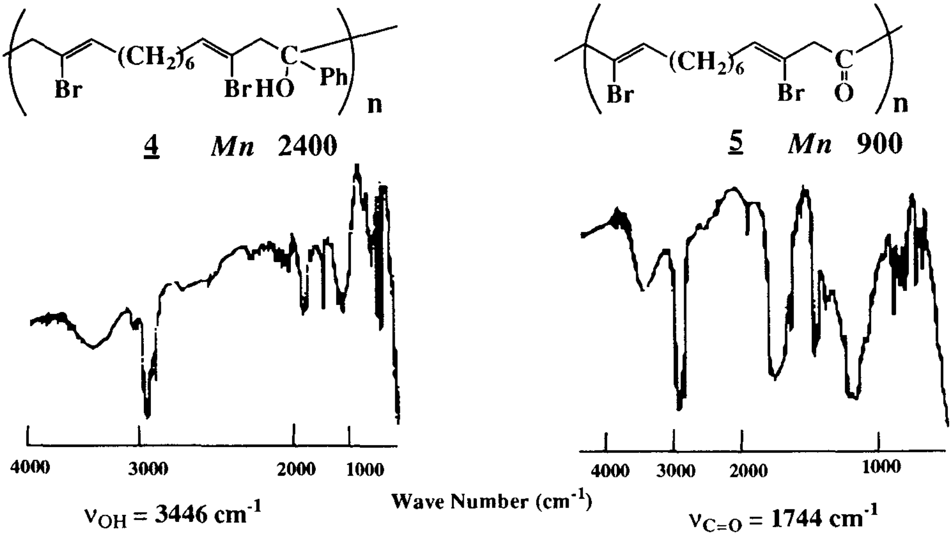
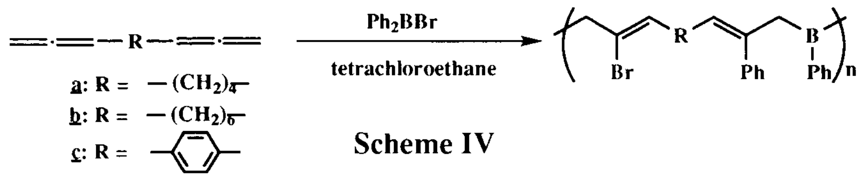


Figure II. IR spectra of polyalcohol (4) and polyketone (5)

The structures of these polymers were supported by ^{1}H-NMR and IR spectra. IR spectra of polyalcohol (**4**) and polyketone (**5**) are represented in Figure II. In IR spectrum of **4**, the specific absorption of alcohol was observed at 3446 cm^{-1} and in that of **5**, C=O streching was observed at 1744 cm^{-1}, respectively. Though the molecular weights of these polymers were relatively low, it was shown that **3b** was converted to the corresponding polyalcohol and polyketone.

When phenyldichloroborane was used as a boron monomer, wide polydispersity was observed, which indicates further phenylboration reaction took place. Making use of this phenylboration reaction, haloboration-phenylboration polymerization of bisallenes by using diphenylbromoborane (**6**) as a boron monomer was examined (Scheme IV).



Scheme IV

First, haloboration-phenylboration polymerization of **2b** under various reaction conditions was performed. The results are summarized in Table III. Reactions were carried out with a trace amount of tetrachloroethane. After feeding monomers at room temperature, the mixtures were gradually warmed up to each reaction temperature and stirred for 3h. When the reaction was carried out at 90°C, no polymerization was observed (run 1). But at 100°C, the polymer was obtained. After the reprecipitation into n-hexane, a brown gum was obtained. This polymeric product was soluble in common organic solvents such as THF, benzene and chloroform and GPC measurement (THF, PSt) showed Mn of the polymer was 2600 (run 2). In the reaction at 110°C, Mn of polymer obtained was 5700 (run 3). However, the reaction at 130°C gave an organoboron gel, which is probably due to further phenylboration (run 4). Phenylboration polymerization of **2b** with triphenylborane was also examined (runs 5-6). But the corresponding polymer was not obtained, presumably due to thermal isomerization of **2b**.

Table III. Haloboration - Phenylboration Polymerization of **2b** under Various Reaction Conditions [a)]

Run	Borane Reagent	Borane / **2b**	temp (°C)	time (h)	*Mw* [b)]	*Mn* [b)]	*Mw / Mn* [b)]	yield(%) [c)]
1	Ph_2BBr	1.21	90	3	No Polymerization			
2	Ph_2BBr	1.15	100	3	4900	2600	1.9	15
3	Ph_2BBr	1.30	110	3	11300	5700	2.0	24
4	Ph_2BBr	1.21	130	3	Gelation			
5	Ph_3B	1.12	130	24	No Polymerization			
6	Ph_3B	1.33	150	24	No Polymerization			

a)(Runs 1 - 4) Reactions were carried out with a trace amount of tetrachloroethane. (Runs 5 - 6) Reactions were carried out in 0.5 M solution of tetrachloroethane. b) GPC (THF), polystyrene standards. c) Isolated yields after reprecipitation into n-hexane.

^{11}B-NMR spectra of the organoboron polymers prepared in runs 2-3 are shown in Figure III. The spectrum of the polymer synthesized in run 2 has a main peak at 46.1 ppm, which indicates relatively linear structure of the polymer. In the case of the polymer prepared in run 3, in addition to previous peak at 46.1 ppm, another peak at 28.3

ppm appears. This peak is attributable to crosslinked structure by further phenylboration.

The results of haloboration-phenylboration polymerization by using various bisallene compounds are summarized in Table IV. The reaction condition was 110°C and 3h in each run. Instead of **2b**, **2a** also gave the corresponding polymer whose Mn was found to be 2000. However, when **2c** was used, a gelation was observed probably because of some thermal isomerizations during the course of polymerization.

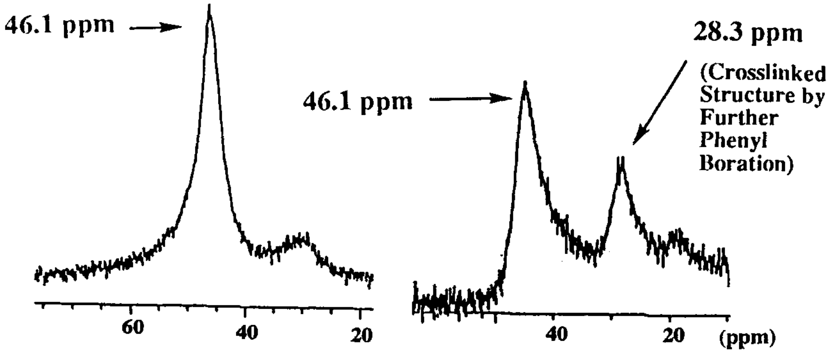
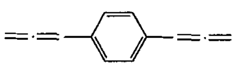


Figure III. ^{11}B-NMR spectra of the organoboron polymers prepared in run 2 (left) and run 3 (right)

Table IV. Haloboration-Phenylboration Polymerization of Various Bisallenes[a]

run	bisallenes (2)		6 / 2	Mw[b]	Mn[b]	yield (%)[c]
1	$=\cdot=—(CH_2)_4—=\cdot=$	(**2a**)	1.12	3200	2000	21
2	$=\cdot=—(CH_2)_6—=\cdot=$	(**2b**)	1.30	11300	5700	24
3		(**2c**)		Gelation		

a) Reactions were carried out with a trace amount of tetrachloroethane at 110°C for 3hours.
b) GPC (THF), polystyrene standards. c) Isolated yields after reprecipitation into n-hexane.

In conclusion, novel reactive polymers were prepared by haloboration polymerization and haloboration-phenylboration polymerization of bisallene compounds. The polymer prepared by haloboration polymerization between tribromoborane (**1**) and 1,2,10,11-dodecatetraene (**2b**) was subjected to chain transformation reaction to give the corresponding polyalcohol and polyketone.

Experimental Section

Materials and Instruments Bisallenes were prepared according to the reported method[9]. Dichloromethane and tetrachloroethane were dried over calcium hydride and distilled. Methanol was dried over magnesium and distilled. Tetrahydrofuran was dried over sodium and distilled before use. Commercially available trimethylsilylbenzene and dichloromethyl methyl ether (DCME) was distilled before use. Tribromoborane and hydrogen peroxide were used without further purification. Phenyllithium/cyclohexane was purchased from Aldrich. 3-Ethyl-3-pentanol lithium alkoxide was prepared by adding an equimolar amount of n-butyllithium/n-hexane to 3-ethyl-3-pentanol at 0°C.

^{1}H-NMR spectrum and ^{11}B-NMR spectrum were recorded in $CDCl_3$ on a JEOL EX-270 instrument. Gel permeation chromatographic analysis was carried out on a Tosoh G3000H_{XI} by using THF as an eluent after calibration with standard polystyrene samples. IR spectrum was obtained on a Perkin Elmer 1600 spectrometer.

Synthesis of Diphenylbromoborane (6) 14.0 ml (80.0 mmol) of trimethylsilylbenzene was added to 4 ml (40 mmol) of tribromoborane (neat) at 0°C for 30 min. After stirring for 1.5 h at 0°C, the reaction mixture was warmed up to room temperature and then refluxed overnight at 125°C. After distillation [105°C (2.0 mmHg)] of the crude product, diphenylbromoborane was obtained as a colorless liquid. Yield 67%. ^{1}H-NMR (δ, ppm) 7.57 (C_6H_5, t, 4H), 7.69 (C_6H_5, t, 2H), 8.09, 8.12 (C_6H_5, d, 4H). ^{13}C-NMR (δ, ppm) 127.8 (C3, C5) 133.0 (C4) 137.4 (C2, C6). 139.7 (C1). ^{11}B-NMR (δ, ppm) 66.7.

Haloboration Polymerization between 1,2,10,11-Dodecatetraene (2b) and BBr_3 (1) To a 1.0 M dichloromethane solution of 1 (1.40g, 0.955 mmol), 2b (137.7 mg, 0.848 mmol) was added with vigorous stirring at -78°C under nitrogen. The reaction mixture was then warmed gradually to room temperature. Methanol (0.3 ml) was added to the reaction mixture at 0°C and stirred for 2h. After the reprecipitation into methanol, 3b (397.2 mg) was obtained as a white gum. yield 97%. ^{1}H-NMR (δ, ppm) 1.29 (=C-C-CH_2-CH_2, 8H), 1.82 (=C-CH_2, CH_2-B, 8H), 3.72 (OMe, 3H), 5.28 (CH=C, 2H).

Reaction between Poly(organoboron halide) and THF To a dichloromethane solution of poly(organoboron halide) (361.0 mg) prepared from 1 and 2b, tetrahydrofuran (2 ml) was added at -78°C, and the reaction mixture was allowed to be warmed to room temperature. After evaporating the solvent, the corresponding polymer was obtained in a quantitative yield. ^{1}H-NMR (δ, ppm) 1.30 (=C-C-CH_2-CH_2, 8H), 1.85 (=C-CH_2, CH_2-B, O-C-CH_2-CH_2, 8H), 3.45 (CH_2Br, 2H), 4.10 (O-CH_2, 2H), 5.28 (CH=C, 2H).

DCME Rearrangement of 3b (Polyalcohol) To a THF (5 ml) solution of polymer 3b (174.7 mg, 0.424 mmol), dichloromethyl methyl ether (0.123 ml, 1.36 mmol) and 3-ethyl-3-pentanol lithium alkoxide/n-hexane (1.60M, 3.1 ml) were added at 0°C. The reaction mixture was stirred at room temperature for 1h. The solvent was evaporated, and the polymer was dissolved in benzene (10 ml). Phenyllithium/cyclohexane (1.82M, 4.0 ml) was added to the solution at -78°C and the reaction mixture was stirred at room temperature for 12h. Then methanol (5 ml), water (3 ml) and 30% hydrogen peroxide (0.3 ml) were added at 0°C. After stirring for 1h at 60°C, the reaction mixture was extracted with benzene and the resulting yellow gum was purified by washing with methanol. Yield 123.5 mg, 68%. ^{1}H-NMR (δ, ppm) 0.92 (=C-C-CH_2-CH_2, 8H), 1.85 (=C-CH_2, CH_2-C-OH, 8H), 3.74 (OH, 1H), 5.20 (CH=C, 2H), 7.37 (Ph, 5H). IR (ν, cm^{-1}) 3446 (-OH).

DCME Rearrangement of 3b (Polyketone) To a THF (10 ml) solution of polymer 3b (161.2 mg, 0.391 mmol), dichloromethyl methyl ether (0.118 ml, 1.30 mmol) and 3-ethyl-3-pentanol lithium alkoxide/n-hexane (1.60M, 1.85 ml) were added at 0°C. The reaction mixture was stirred at room temperature for 1h. Then methanol (3 ml), sodium hydroxide (0.2 g) and 30% hydrogen peroxide (0.5 ml) were added at 0°C. After stirring for 1h at 60°C, the reaction mixture was extracted with benzene and purified by washing with ether. <u>**5**</u> was obtained as a brown solid. Yield 51%. ^{1}H-NMR (δ, ppm) 0.95 (=C-C-CH_2-CH_2, 8H), 1.86 (=C-CH_2, 4H), 2.21 (CH_2-C=O, 4H), 5.21 (CH=C, 2H). IR (ν, cm^{-1}) 1744 (C=O).

Haloboration-Phenylboration Polymerization of <u>2b</u> To a 1.0 M tetrachloroethane solution of <u>**6**</u> (340.6 mg, 1.39 mmol), <u>**2b**</u> (172.8 mg,1.07 mmol) was added at room temperature. The reaction mixture was gradually warmed up to 110°C and was stirred for 3h. After the reprecipitation into n-hexane, the corresponding polymer was obtained as a brown gum (99.5 mg). Yield 24%. ^{1}H-NMR (δ, ppm) 1.28 (=C-C-CH_2-CH_2, 8H), 1.86 (=C-CH_2, CH_2-B, 8H), 5.19 (CH=C, 2H), 7.37 (Ph, 5H).

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