Polyhomologation: The Living Polymerization of Ylides

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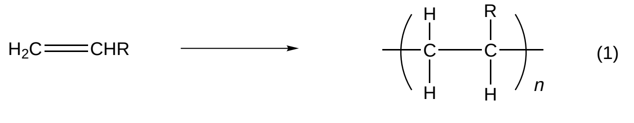
Abstract: The polymerization of dimethylsufoxonium methylide to produce linear polymethylene polymers is described. The reaction is catalyzed/initiated by trialkylboranes and gives organoboron star polymers as the primary product. The reaction is a living polymerization, providing control over molecular weight and functionality at the polymer chain ends. A variety of novel polymethylene architectures are available by this methodology.

Keywords: organoboranes · polymerizations · polymethylene · telechelics · ylides

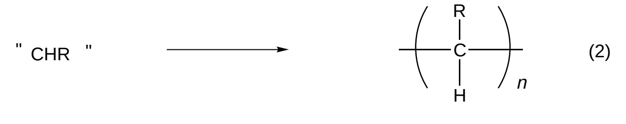
Introduction

It is difficult to imagine a world without synthetic polymers. The most important commercial polymers include polyolefins such as polystyrene, polypropylene, polyethylene, and polyvinylchloride. Annual worldwide production of polyethylene alone exceeds 100 billion pounds in weight![1] The products that are fabricated from these materials are ubiquitous in contemporary society.

Polyolefins contain a carbon backbone that is synthesized by the polymerization of alkenes. The macromolecular carbon chain is built up two carbons at a time [Eq. (1)]. The raw materials for these commodity plastics are derived from petroleum. Although cheap and abundant at present, the supply of petroleum is finite and long-term strategies for their replacement will be necessary.[2]



$$\mathrm{H_2C{=}CHR} \longrightarrow \left(\mathrm{CH_2{-}CHR} \right)_n \qquad (1)$$



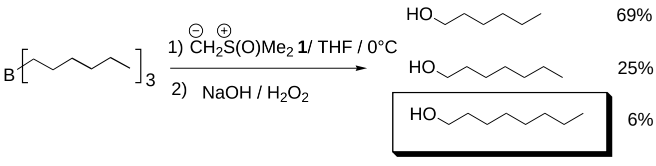
$$\text{" CHR "} \longrightarrow \left(\mathrm{CHR} \right)_n \qquad (2)$$

We have been exploring alternative approaches to synthesize carbon backbone polymers. Novel strategies for their synthesis can lead to new polymer architectures in addition to telechelics and copolymers that are not readily available by existing olefin-polymerization methods. In addition, research in this area may eventually lead to useful non-petroleum based technologies for the production of commodity polymers.

Our studies have focused on nontraditional monomers as the carbon source for these polymers. We have discovered that sulfur-based methylene ylides can be polymerized by alkylboranes. Unlike conventional olefin polymerization, the polymer chain is built up *one carbon at a time* [Eq. (2)]. This new reaction, which we have termed *polyhomologation*[3] has the characteristics of a living polymerization, allowing control over molecular weight and functionality at either end of the polymer chain.[4]

Background

Our initial effort drew from the work of Tufariello and coworkers[5] who studied methods for the homologation of trialkylboranes. They noted that the ylide dimethylsulfoxonium methylide (**1**)[6] underwent reaction with trihexylborane. Upon oxidative workup, a mixture of C_6, C_7, and C_8 alcohols were formed (Scheme 1). Although practical synthetic methodology did not emerge from this particular reaction, it demonstrated that the homologation reaction could be repeated more than once.



Scheme 1. Reaction of trihexylborane with **1**.

Mechanistically, the homologation reaction in Scheme 1 involves initial attack of ylide **1** on the alkylborane to form a borate complex. The complex then undergoes a 1,2-migration of the alkyl group to produce a homologated alkylborane and a molecule of dimethyl sulfoxide [Eq. (3)].

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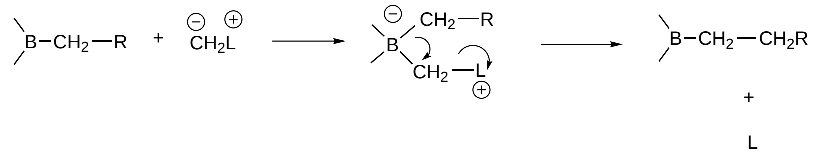


(3)

The homologated alkylborane product is then available to react with additional ylide. The minor amount of C_8 bishomologated product produced as a side product in the original report of this reaction are consistent with this mechanism.

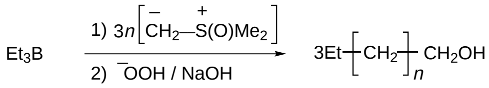
In the absence of competing nucleophiles, the reaction *in principle* may be repeated many times. Repetitive homologation could be used for synthesis of long hydrocarbon chains (polymethylene). To evaluate this possibility we first examined the reaction of simple alkylboranes with a 200-fold excess of ylide. It was observed that the addition of triethylborane to a THF solution of dimethylsulfoxonium methylide at 40 °C led to consumption of the ylide within 10 min. During the course of the reaction the solution became cloudy. Concentration, then treatment with basic peroxide ($NaOH/H_2O_2$, THF, H_2O) produced a white waxy solid in >95% yield. Spectral properties of the product were consistent with a hydroxyl-terminated long-chain alkane.[7] Since the hydrocarbon chain is built up one carbon at a time, the new material is a polymethylene oligomer.[8] Linear hydrocarbons, such as polymethylene with $>C_{30}$, are insoluble at room temperature and are only soluble in a limited number of solvents (i.e., toluene) at elevated temperatures. To ensure homogeneity of the reaction, toluene solutions of ylide **1**, preheated to 70–80 °C, were treated with triethylborane. The ylide was rapidly consumed (5 min). Following concentration and oxidative workup, a quantitative yield of hydroxyl-terminated polymethylene was obtained (Scheme 2).[9]

The average molecular weight was found to be very close to the initial ratio of (ylide/trialkylborane)/3. In three experiments with ratios/3 of 50, 117, and 232, the experimentally determined degree of polymerization (DP; NMR end-group analysis, gel permeation chromatography (GPC), polyethylene standards) was 48, 108, and 231, respectively (Table 1). To account for the molecular weight of the linear alcohol products, all three alkyl groups on boron must participate in the reaction. The initial product, therefore, is a star polymethylene organoborane **2**. The reaction is illustrated Scheme 2.

The strict relationship between molecular weight and reaction stoichiometry is consistent with a *living polymerization*.[10] The absence of a termination step is reasonable, since the "living end" of this polymer is a trialkylborane, which should be stable under the reaction conditions. DMSO, the only biproduct in the reaction, does not form stable complexes with trialkylboranes. Further support for the living character of polyhomologation was found from the polydispersities (M_w/M_n) of the reaction products. Representative values range from 1.01 to 1.17. Interestingly, some of the lowest polydispersities are obtained from low molecular weight oligomers.

The trialkylborane-initiated polymerization of dimethylsulfoxonium methylide followed by oxidative cleavage of the carbon–boron bond produces perfectly linear polymethylene.

Table 1. Molecular weight and polydispersity of oligomeric hydroxyl-terminated polmethylene **3**.



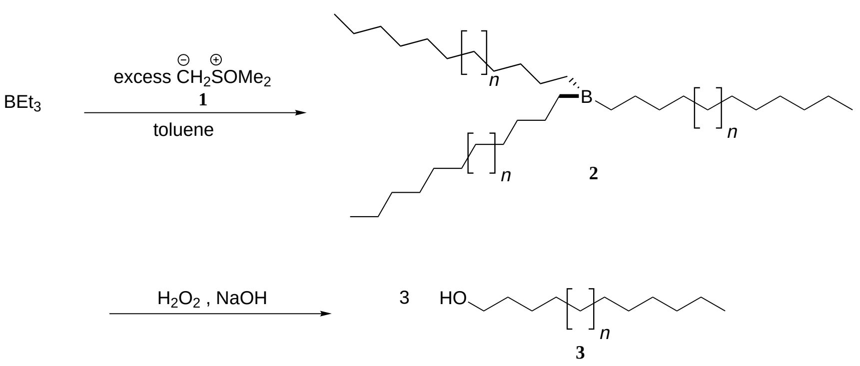
Polymer	DP (calcd from feed ratio)	DP (GPC)[a]	M_n (GPC)	PD (GPC)
$Et(CH_2)_nCH_2OH$	50	48	727	1.04
	117	108	1563	1.05
	232	231	3287	1.17

[a] Analysis performed on a high temperature GPC with *o*-xylene as the mobile phase (1 mL min^{-1}) at 105 °C. Pure hydrocarbons and narrow molecular weight polyethylene standards were used for calibration.

The molecular weight is controlled from the initial ratio of ylide to trialkylborane. The reaction has been used to prepare polymethylene samples with molecular weights that range from several hundred to over one hundred thousand.[11]

Functional Polymethylenes. Telechelics and Terminal Functionalized Polymers

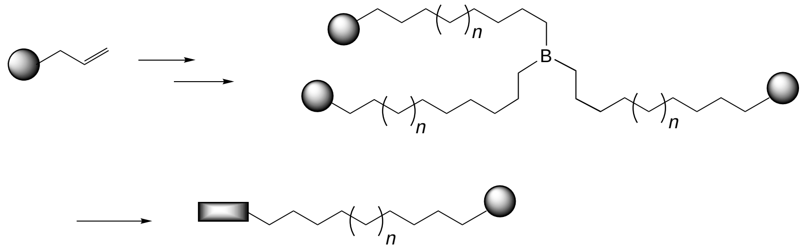
The primary products of the polyhomologation reaction, oligomeric and polymeric organoboranes, are amenable to a number of synthetic transformations that introduce functionality at the terminal position of the polymethylene chain. As illustrated in the previous example, peroxide cleavage of the carbon–boron bonds in star **2** results in formation of hydroxyl-terminated linear polymethylene **3** (Scheme 2). Oxidative cleavage is only one of many transformations of the carbon–boron bond. The rich chemistry of this functional group permits the polymethylene-chain end to be terminated



Scheme 2. Reaction of BEt_3 with **1**.

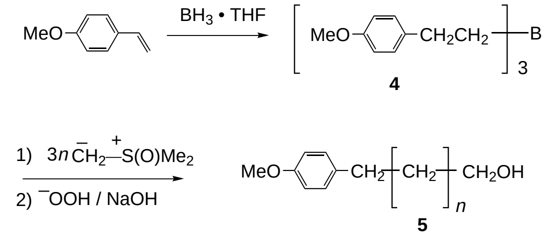
with a number of functional groups, including hydrogen (alkanes), amines, halogens, and carbon–metal bonds.[12]

The alkyl group of the organoborane initiator winds up at the *beginning* of the polymethylene chain. Diverse organoboranes are available by either hydroboration of alkenes or by direct substitution of functional boranes.[13] Following polyhomologation, transformation of the carbon–boron bond introduces functionality at the *end* of the polymethylene chain. Thus, the polyhomologation of organoboranes can be used to synthesize telechelic polymethylene derivatives (Scheme 3).[9]



Scheme 3. Schematic representation of the synthesis of telechelic polymethylene derivatives.

The process is illustrated by the preparation of α-*p*-methoxyphenyl-ω-hydroxypolymethylene (Scheme 4). The initiator, tris(*p*-methoxyphenylethyl)borane (**4**), was prepared by hydroboration of *p*-methoxystyrene.[14] The organoborane was then rapidly added through a syringe to a preheated toluene solution of ylide. Following consumption of ylide (5 min), concentration and oxidation, a quantitative yield of α-*p*-methoxyphenyl-ω-hydroxypolymethylene **5** was obtained. For samples prepared with an initial ylide/alkylborane ratio of 58:1, the average DP calculated by field desorption mass spectrometry (FDMS) is 66. The polydispersity (M_w/M_n) of this sample was 1.02 (GPC; polyethylene standards) and 1.01 (FDMS). A representative field desorption mass spectrum is shown in Figure 1. Mass spectrometry and GPC also reveal that a small amount of product (<5%) is found *on occasion*, at approximately twice the mass of the major product. This may arise from the reaction of trace O_2 with organoboranes *after* polyhomologation. This reaction can produce alkyl radicals which can dimerize. We are currently investigating this reaction to verify the origin of this minor product and the mechanism of its formation.



Scheme 4. Reaction scheme for the preparation of α-*p*-methoxyphenyl-ω-hydroxypolymethylene.

Novel Polymethylene Architectures

Star-branched polymethylene: Trialkylboranes undergo a number of "stitching" transformations that result in the transfer of the three alkyl groups on boron to a common carbon atom.[15] When these reactions are carried out on tris-polymethylene organoboranes, novel tripodal tris-polymethylene carbinols are formed.[16]

The example below illustrates this concept. The synthesis of polymethylene carbinol **6** was accomplished by the polyhomologation–chain-stitching–oxidation sequence shown in Scheme 5. Triethylborane was introduced in a preheated solution of dimethylsulfoxonium methylide/toluene under N_2. The ylide was consumed in three minutes. α,α-Dichloromethyl methyl ether (DCME) was added to the heated mixture followed by dropwise addition of a hexane solution of lithium 1,1-diethylpropoxide.[17] After 2 h at 40 °C the resulting polymethylene derivative was oxidized to afford tripodal tris-polymethylene carbinol **6**. In experiments where the

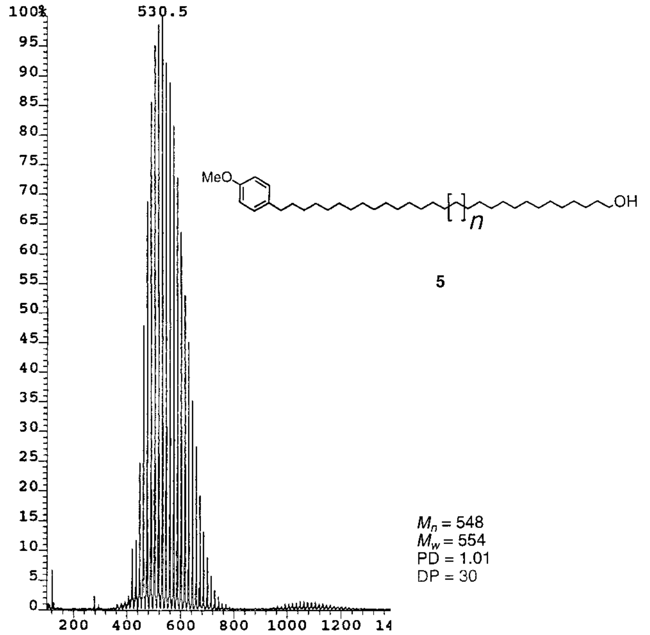
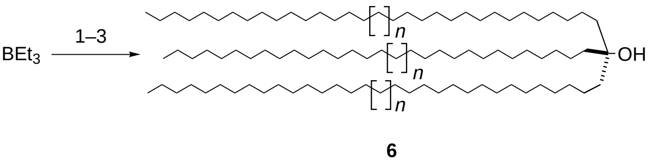


Figure 1. FDMS mass spectrum analysis of telechelic polymethylene.



Scheme 5. Polyhomologation–chain-stitching–oxidation sequence. Reaction conditions: 1) 3*n***1**, toluene, 50 °C; 2) $CHCl_2OMe$, $LiOCEt_3$, 40 °C; 3) H_2O_2, NaOH.

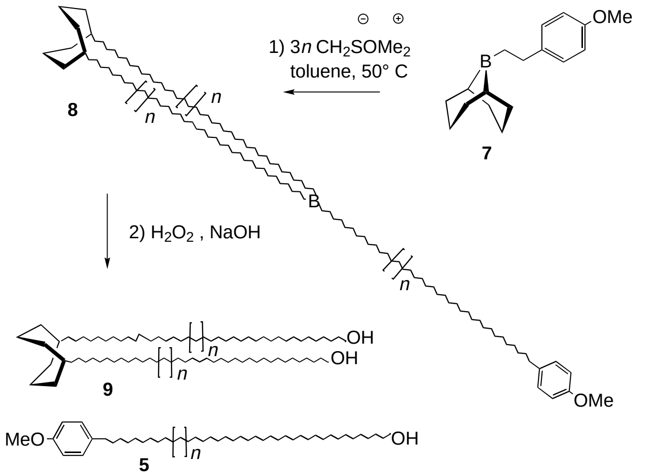
molar ratio of ylide to organoborane varied from 25, 60, 90, and 120, the experimentally determined number of average molecular weights (M_n) of the carbinol product were 530, 775, 1682, and 1982 respectively, in close agreement with the calculated molecular weights (Table 2).[16] The polydispersities (PDs) ranged from 1.02 to 1.13. The branched polymethylene architectures produced by the polyhomologation–carbon-stitching sequences provide access to structures that are not readily available by conventional ethylene polymerization.

Table 2. GPC analysis of polymethylene carbinol **6**.

	initiator: ylide	M (calcd)[a]	M_n[b]	M_w	PD[c]
1	25	453	530	541	1.02
2	60	873	775	817	1.05
3	90	1380	1682	1853	1.10
4	120	1801	1982	2243	1.13

[a] The calculated molecular weight is based on theoretical degree of polymerization from initial ylide to borane ratio. [b] M_n (number average molecular weight) was determined by GPC analysis. [c] PD = (M_w/M_n) is also determined by high temperature GPC.

Ring expansion of cyclic and polycyclic organoboranes: Particularly interesting architectures may be synthesized by polyhomologation of bridged bicyclic organoboranes.[16] A case in point is the bridged bicyclic organoborane 9-BBN. This molecule has two carbon–boron bond types that can undergo migration. In reactions that bear mechanistic similarities to polyhomologation, such as oxidation with amine oxides, selective bridgehead carbon–boron migration is observed.[18] Regardless of the outcome, polyhomologation of 9-BBN derivatives can result in formation of novel polymethylene architectures. The experimental findings are summarized in Scheme 6.



Scheme 6. Formation of novel polymethylene architectures from the polyhomologation of 9-BBN derivatives.

The starting material, *B*-*p*-methoxyphenyl-9-BBN **7**, is prepared by the hydroboration of *p*-methoxystyrene with 9-BBN. The polyhomologation reaction was performed by the addition of a solution of **7** in THF to the ylide **1** in toluene at 50 °C (Scheme 6). The ylide was rapidly consumed. Subsequent oxidative cleavage of the carbon–boron bonds yielded two polymethylene structures. Interestingly, since narrow distributions of oligomeric chains are produced, the two polymethylene structures can be separated by simple SiO_2 chromatography. Separation of telechelic **5** from **9** was achieved at 55 °C by using a 8:2:1 toluene/hexane/EtOAc solvent combination. The GPC and NMR analysis of the resulting product confirmed a 1:1 mixture of α-*p*-methoxyphenyl-ω-hydroxypolymethylene **5** and *cis*-1,5-*bis*-(α-hydroxy-polymethylene) cyclooctane **9**. These structures are derived from a grossly expanded 9-BBN **8**, (Scheme 6).

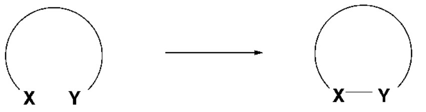
Thus, despite what might initially be a selective migration of the bridgehead carbon–boron bonds, the bridged bicyclic initiator **7** experiences more or less statistical insertions into all carbon–boron bonds; this results in an "exploded" borabicyclic structure. Despite differences in the initial rate of insertion, the molecular weight of **9** is approximately twice that of **5**. Furthermore, the molecular weights of **5** are directly related to the ratio of ylide **1** to initiator **7** (Table 3).[15]

Table 3. Summary of GPC analysis of α-*p*-methoxyphenyl-ω-hydroxypolymethylene carbinol **5** produced by the polyhomologation and oxidative cleavage of **7**.

	initiator: ylide	M (calcd)[a]	M_n[b]	M_w	PD[c]
1	30	897	714	776	1.08
2	45	1066	758	844	1.11
3	90	1698	1349	1545	1.14
4	120	2219	1741	2155	1.20
5	150	2539	2784	3313	1.19

[a] The calculated molecular weight is based on theoretical degree of polymerization from initial ylide to borane ratio. [b] M_n (number average molecular weight) was determined by GPC analysis. [c] PD = (M_w/M_n) was also determined by GPC.

Synthesis of macrocyclic oligomers and polymers: General strategies for the synthesis of macrocycles are quite limited.[19] The basic approach relies on ring closure of an α,ω-difunctional linear precursor under conditions of high dilution [Eq. (4)]. The polyhomologation reaction provides a new strategy for their synthesis.[20] Repetitive methylene insertions into the carbon–boron bond of boracyclanes generate macrocyclic rings [Eq. (5)]. These macrocyclic organoboranes can be elaborated to carbocyclic rings and other derivatives.



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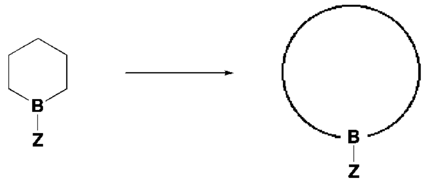

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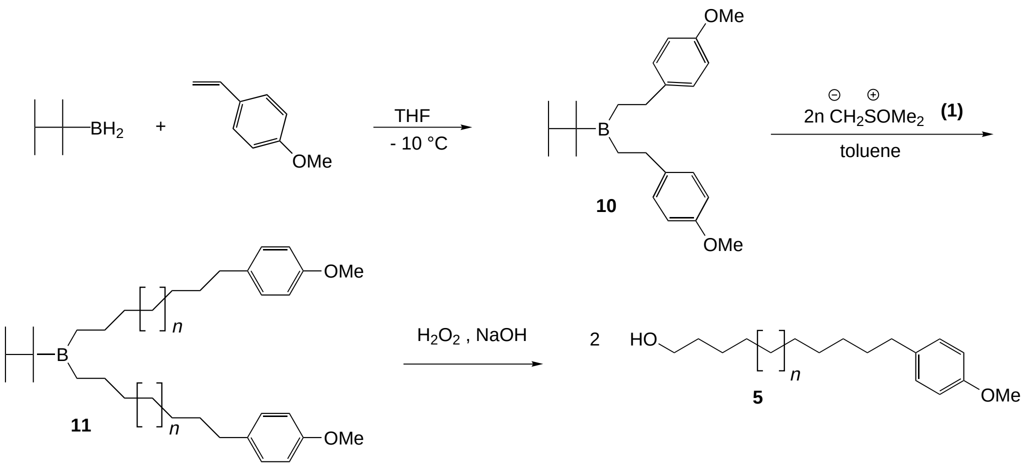


Scheme 7. Reaction scheme showing the use of thexyl as a blocking group.

Boracyclanes are readily prepared by hydroboration of dienes. However, since all three boron–carbon bonds in trialkylboranes undergo polyhomologation, it would be desirable to orchestrate selective migration of the ring carbon–boron bonds. To this end we chose thexylborane as the hydroborating agent. The thexyl group has been shown to exhibit a low migratory aptitude in rearrangements of organoboranes.[21] This low migratory aptitude could be capitalized on to allow *exclusive* ring expansion. To verify the use of the thexyl group as a blocking ligand, thexylborane was treated with two equivalents of *p*-methoxystyrene in THF at −10 °C (Scheme 7). Thexyl-[bis(methoxyphenylethyl)]-borane **10** was added to 50 molar equivalents of dimethylsulfoxonium methylide (**1**) at 0 °C. Following ylide consumption (<10 min), oxidation (NaOH, H_2O_2) provided α-*p*-methoxybenzene-ω-hydroxypolymethylene **5** in 85 % yield.[20] The product was free of thexyl-terminated polymethylene. Its absence confirms the low migratory aptitude of the thexyl group in the polyhomologation reaction; this effectively restricts the number of propagating polymethylene chains on boron from three to two, that is, exclusive formation of **11**.

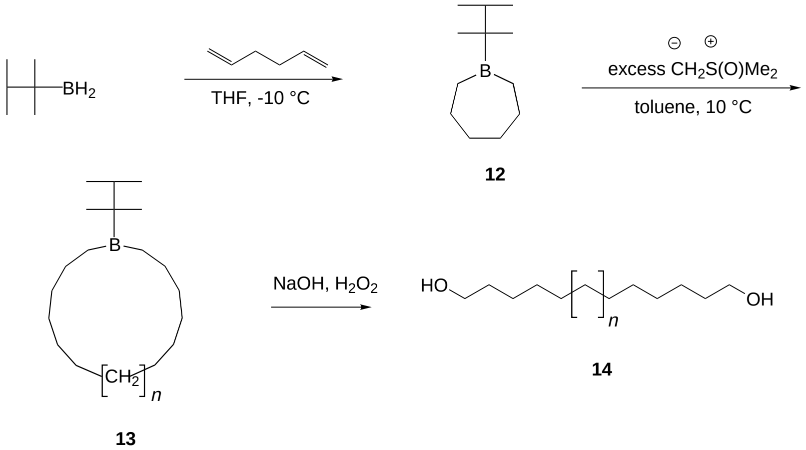
Incorporation of a nonmigrating thexyl substituent as the third ligand in a *boracycle* allows for selective ring enlargement. *B*-Thexylboracycloheptane **12** was prepared by the hydroboration of 1,5-hexadiene with thexylborane in THF at −10 °C (Scheme 8). The polyhomologation reaction was run by using an excess of ylide **1** in toluene at ~5–10 °C. Verification of exclusive ring expansion to boracycle **13** was obtained by oxidization to the α,ω-polymethylene **14**. No thexyl-containing polyhomologated product was observed and the overall yield of **14** for the hydroboration, polyhomologation, oxidation sequence was >90 %.

The non-participation of the thexyl blocking group allows control of the ring expansion of boracycle **12**. This was established by pairs of experiments that employed different ratios of ylide **1** to thexylboracycle **12**. Following polyhomologation to **13** and oxidative cleavage, the molecular weights of diol **14** were determined by a combination of GPC and NMR end-group analysis. The experimentally determined ratio of molecular weights showed a strong correspondence to the ratios calculated on the basis of the ratio of **1**/**12** (Table 4). Thus, the average ring size is controlled by the ratio of these two reagents.

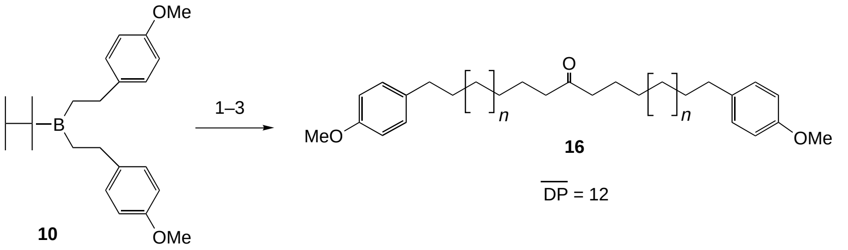
Table 4. Molecular weight and PD for α,ω-dihydroxylpolymethylene **14** produced from the oxidative cleavage of thexylboracycle **13**.

Run	M_n	PD	Calcd ratio of molecular weights (b/a)[a]	Found (b/a)[b]
1a	705	1.07	1.7	1.6
1b	1180	1.29		
2a	1139	1.21		
2b	2023	1.63	1.8	1.8
3a	469			
3b	1127	1.60	2.3	2.4

[a] Ratio of molecular weights of **14** between runs a and b calculated for the molar ratios of **1**/**12**. [b] Experimentally determined ratios.



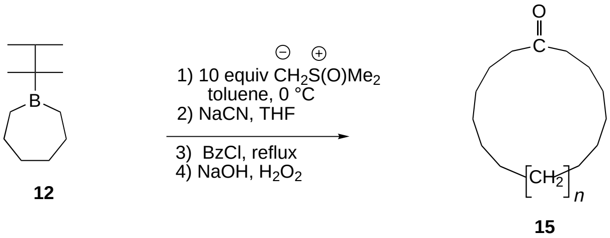
Scheme 8. Preparation of compounds **12**–**14**.



10 **16**

Scheme 10. Preparation of compound **16**. Reaction conditions: 1) 20 equiv **1**, toluene, 0 °C; 2) $CHCl_2OMe$, $LiOCEt_3$; 3) H_2O_2, NaOH.

The macrocyclic organoboranes may be transformed directly to carbocyclic rings.[22] The utility of this new chemistry is demonstrated by synthesis of a distribution of macrocyclic ketones. The molecular weights incorporate members of the musk odorant class.[23] In one experiment, *B*-thexylborocane **12** was added to ten equivalents of ylide in THF at room temperature. After ylide consumption, the expanded boracycle was treated with sodium cyanide, followed by benzoyl chloride then peroxide oxidation (Scheme 9). The yield of cyclic ketone **15** was approximately 30 %. On the basis of the ratio of integrated intensities of methylenes α to the carbonyl to those of the ring methylenes, the calculated DP = 20. The distribution of ketone macrocycles is shown in the gas chromatograph of the reaction mixture (Figure 2). The identity of the individual peaks was established by high resolution GC mass spectrometry. The most abundant molecular ion ($[M]^+$ 322.3222) corresponds to a twenty-one member cyclic ketone (322.3235). The molecular ions of the surrounding peaks were separated by m/z 14.03. The molecular weights, calculated from the mass spectral data, are $M_n = 290$ and $M_w = 295$ (PD = 1.02).



12 **15**

Scheme 9. Preparation of compound **15**.

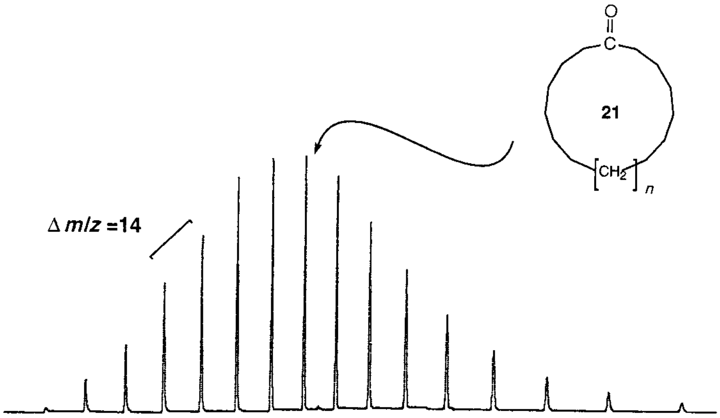


Figure 2. The distribution of ketone macrocycles from the gas chromatograph of the reaction mixture.

The *B*-thexyl-*B*,*B*-bis-(*p*-methoxyphenethyl)borane **10** may also be converted to linear polymethylene ketones. This was achieved by polyhomologation of **10** followed by treatment with α,α-dichloromethyl methyl ether and lithium 1,1-diethylpropoxide in toluene. After 30 min, the reaction mixture was oxidized under alkaline peroxide conditions (Scheme 10). *Bis*-(*p*-methoxyphenyl) polymethylene ketone **16** was isolated in 65 % yield. In one example, a 20:1 ratio (calculated DP = 10), gave ketone **16** with a DP = 12. Mass spectral analysis of the product gave $M_n = 635$ and $M_w = 640$ (PD = 1.01).

Summary

A new approach to the synthesis of carbon-backbone polymers has been described. Organoboranes have been found to catalyze the polymerization of dimethylsulfoxonium methylide. Unlike conventional olefin polymerization, the polymer chain is built up *one carbon at a time*. This new reaction, which we have termed *polyhomologation*, exhibits characteristics of a living polymerization, allowing control over molecular weight and functionality at either end of the polymer chain. The reaction may also be used for synthesis of novel polymethylene architectures and macrocyclic rings.

Acknowledgments

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[3] The term polyhomologation is used to distinguish this polymerization from olefin polymerization. The polymer is built up one CH_2 unit at a time (homologation) as opposed to two carbons at a time for olefin polymerization. The two materials can be differentiated by mass spectrometry. Polymethylene spectra show peaks separated by 14 mass units, in polyethylene, the peaks are separated by 28 mass units.

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