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The Boron-Catalyzed Polymerization of Dimethylsulfoxonium Methylide. A Living Polymethylene Synthesis

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Abstract: Trialkyl and aryl organoboranes catalyze the polymerization of dimethylsulfoxonium methylide (**1**). The product of the polymerization is a tris-polymethylene organoborane. Oxidation affords linear telechelic α-hydroxy polymethylene. The polymer molecular weight was found to be directly proportional to the stoichiometric ratio of ylide/borane, and polydispersities as low as 1.01−1.03 have been realized. Although oligomeric polymethylene has been the most frequent synthetic target of this method, polymeric star organoboranes with molecular weights of 1.5 million have been produced. The average turnover frequency at 120 °C in 1,2,4,5-tetrachlorobenzene/toluene is estimated at $>6 \times 10^6$ g of polymethylene (mol boron)$^{-1}$ h^{-1}. The mechanism of the polyhomologation reaction involves initial formation of a zwitterionic organoborane•ylide complex which breaks down in a rate-limiting 1,2-alkyl group migration with concomitant expulsion of a molecule of DMSO. The reaction was found to be first order in the borane catalyst and zero order in ylide. DMSO does not interfere with the reaction. The temperature dependence of the reaction rate yielded the following activation energy parameters (toluene, $\Delta H^{\ddagger} = 23.2$ kcal/mol, $\Delta S^{\ddagger} = 12.6$ cal deg/mol, $\Delta G^{\ddagger} = 19.5$ kcal/mol; THF, $\Delta H^{\ddagger} = 26.5$ kcal/mol, $\Delta S^{\ddagger} = 21.5$ cal deg/mol, $\Delta G^{\ddagger} = 20.1$ kcal/mol).

Introduction

Carbon backbone polymers comprise one of the world's largest sources of synthetic materials.[1] They are prepared by the polymerization of olefins, which are derived from petroleum. Olefin polymerization reactions build the carbon backbone two-carbon atoms at a time. Catalysts of exceptional efficiency have been developed for these purposes, and remarkable control over many of the key variables that influence physical properties and polymer performance has been achieved.[2] Despite these advances, there are still synthetic challenges that remain. For example, many olefins, particularly the more highly substituted derivatives, do not polymerize; their polymers are unknown. The direct synthesis of many types of polymer architectures,[3] for example giant macrocyclic rings, cannot be readily achieved by olefin polymerization. In addition, there are many functional groups that are not compatible with existing catalysts, so new methods for their synthesis are needed. Furthermore, despite significant recent developments,[4] controlled synthesis of copolymers of the more important commodity polymers such as poly(ethylene-*b*-styrene)[5] remains a challenge.

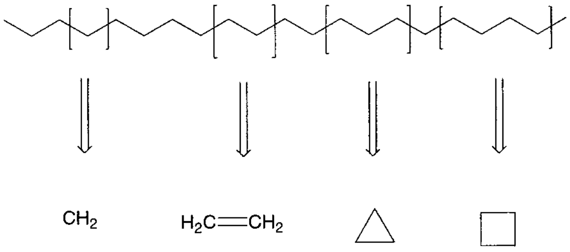

Figure 1. Possible disconnections of a simple linear hydrocarbon polymer.

Although olefins are the most obvious and practical synthetic building blocks for the carbon backbone, alternative methods for synthesizing carbon chains offer the potential for novel solutions to some of these aforementioned synthetic challenges. If one lifts the restriction of the C2 carbon source, new approaches utilizing C1, C3, C4, or larger building blocks can be envisioned, providing of course, suitable building blocks and catalysts can be found (Figure 1).[6] These novel approaches, employing completely different chemistries, may not suffer the same limitations of olefin polymerization.

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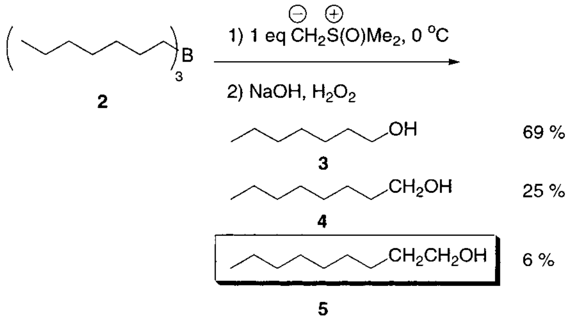
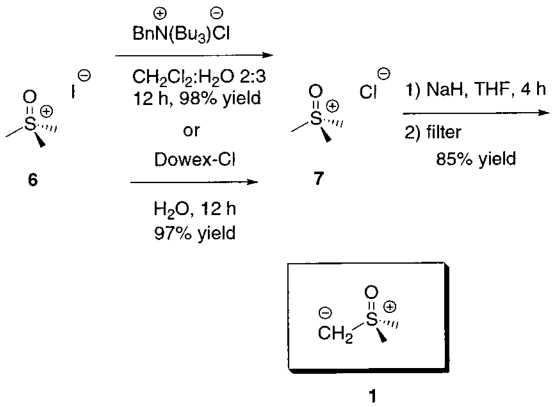
Scheme 1. Products from the Reaction of Equimolar Amounts of Ylide **1** and Borane **2** Following Oxidative Cleavage[11]



Scheme 2. Synthesis of Dimethylsulfoxonium Methylide (**1**)



We have been exploring nonolefin routes for the synthesis of carbon backbone polymers.[7] These routes involve repetitive carbon−carbon bond forming reactions that extend the carbon chain *one carbon at a time*. The parent material in this family of hydrocarbon polymers is polymethylene. The history of this polymer dates back over 100 years. Bamberger and Tirchner[8] noted that long standing etheral solutions of diazomethane form a white precipitate that was analyzed for the formula $(CH_2)_x$. Substantial research has been directed toward the catalyzed decomposition of diazomethane since this initial observation. High molecular weight polymethylene (3.3×10^6 D)[9] is produced by a number of Lewis acids,[10] including copper salts and BF_3. Our efforts have been directed at developing new methods for the synthesis of simple linear hydrocarbon polymers. This study has led to the discovery of a new, living polymerization of dimethylsulfoxonium methylide (**1**). The chemistry of this reaction is described below.

Results and Discussion

The homologation of organoboranes with dimethylsulfoxonium methylide (**1**) was first reported by Turfariello and coworkers (Scheme 1).[11] The reaction of equimolar amounts of ylide **1** and tri-*n*-heptylborane (**2**) followed by oxidative cleavage of the carbon−boron bonds produced three products, heptanol (**3**) (69%), octanol (**4**) (25%), and small amounts of decanol (**5**) (6%). The homologated products arise from methylene insertion into the carbon−boron bond. The formation of a doubly homologated product **5** was noteworthy and prompted our investigation of this reaction using a large excess of ylide **1**. We speculated that multiple homologations with **1** could result in polymethylene formation.

Ylide **1** was synthesized according to Scheme 2. Trimethylsulfoxonium iodide (**6**) was converted to trimethylsulfoxonium chloride (**7**) via ion-exchange with benzyltributylammonium chloride. The chloride **7** was recrystallized from MeOH.[12] Alternatively, aqueous solutions of **6** can be passed through an ion-exchange resin of Dowex-Cl. Both procedures convert the readily available iodide salt **6** to the chloride salt **7**. It is advantageous to use the chloride salt **7** since the stability and solubility are higher than those of the iodide **7**. The ylide **1** is produced by refluxing a heterogeneous mixture of trimethylsulfoxonium chloride (**7**) and sodium hydride in THF or toluene for 4 h. The inorganic salts are filtered to afford a homogeneous solution of ylide **1** of approximately 0.6 molar. Ylide **1** is stable and can be stored at −20 °C for greater than 3 weeks. The ylide concentration is established by quenching an aliquot in water and titrating with standardized HCl.

In preliminary studies, triethylborane was added to a solution of 100 equiv of ylide **1** in THF at 40 °C. The solution became cloudy, and a white precipitate formed within 10 min. Hydrolysis of one drop of the reaction mixture in water containing phenolphthalein indicated complete consumption of ylide **1**. The organoborane was oxidized with basic hydrogen peroxide to afford a quantitative yield of α-hydroxypolymethylene (**8**) (eq 1). The NMR and IR spectroscopic properties of this product were consistent with a linear, terminal alcohol. Interestingly, analysis of the reaction product by gel permeation chromatography (GPC) revealed a broad, polymodal distribution of polymers. We believe that the turbidity that developed during the reaction in THF was associated with the aggregation and precipitation of extended polymethylene chains. Hydrocarbon chains >30 carbons are not soluble in THF at any temperature. It is likely that the precipitation of growing polymer chains resulted in the broad distribution of molecular weights since heterogeneous polymerizations exhibit varying activities of catalytic centers brought about by growing polymer chains.[13]

$$\mathrm{Et_3B} \xrightarrow[\text{(2) H}_2\text{O}_2\text{, NaOH}]{\text{(1) 100 equiv of ylide, 40 °C}} \underset{\mathbf{8}}{\mathrm{Et{-}(CH_2)_{\mathit{n}}{-}OH}} \tag{1}$$

In an effort to develop homogeneous polymerization conditions, ylide **1** solutions in toluene[14] were prepared. Linear polyethylene has significant solubility in toluene at elevated temperatures. A typical polymerization consisted of injecting 27 μL of a 1 molar solution of triethylborane (27 μmol) into 14 mL of 0.58 molar ylide **1** (8.1 mmol, theoretical degree of polymerization (DP_{th}) = 100) in toluene at 70 °C. The reaction remained homogeneous. Sampling the reaction mixture after 5 min indicated complete consumption of ylide **1**. The toluene was removed in vacuo, and THF, hydrogen peroxide, and

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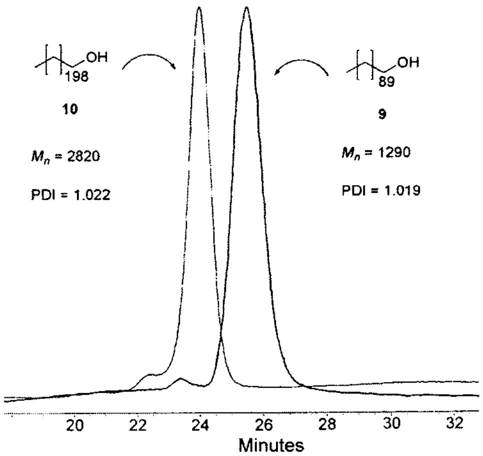
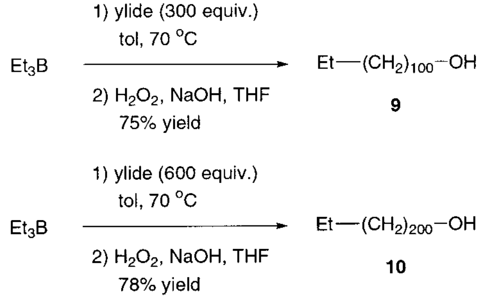
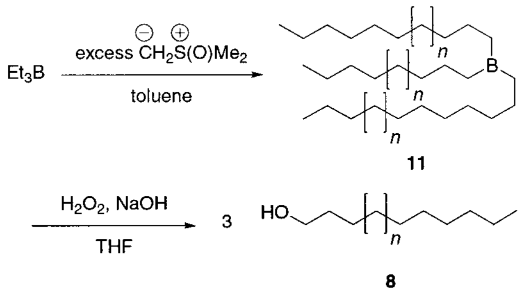


Figure 2. Superimposition of GPC traces for α-hydroxypolymethylene (**9**) and (**10**).

Scheme 3. Synthesis of α-Hydroxypolymethylene **9** (DP_{th} = 100) and **10** (DP_{th} = 200)



Scheme 4. Triethylborane-Initiated Polyhomologation of Ylide **1** Produces an Intermediate 3-Arm Star Polymethylene **11** (Oxidation Affords Linear α-Hydroxypolymethylene **8**)



sodium hydroxide were added. The resulting polymer was isolated by precipitation with acetonitrile and filtration to afford α-hydroxypolymethylene (**9**) in 75% yield (Scheme 3).

The experiment described above was repeated with one-half of the borane initiator. The reaction of 13.5 μL of a 1 molar solution of triethylborane (13.5 μmol) and 14 mL of 0.58 molar ylide **1** (8.1 mmol, $DP_{th} = 200$) was used to afford α-hydroxypolymethylene (**10**) in 78% yield (Scheme 3). GPC analysis for both **9** ($DP_{exp} = 89$, $M_n = 1290$, PDI = 1.02) and **10** ($DP_{exp} = 198$, $M_n = 2820$, PDI = 1.02) revealed a narrow, monodisperse polymer distribution with an experimental molecular weight in agreement with the calculated molar ratio of [ylide]/3[Et_3B] (Figure 2). The stoichiometry of the reaction between ylide **1** (3*n* equiv) and triethylborane (1 equiv) is consistent with the formation of an intermediate 3-arm star polymethylene (DP = 3*n*) (Scheme 4). Oxidation affords 3 equiv of α-hydroxypolymethylene (**9**) and (**10**) with DP = *n*. The strict correspondence between stoichiometry and molecular weight in the preceeding examples is consistent with a rapid initiation and the absence of termination reactions in the polymerization of ylide **1**.

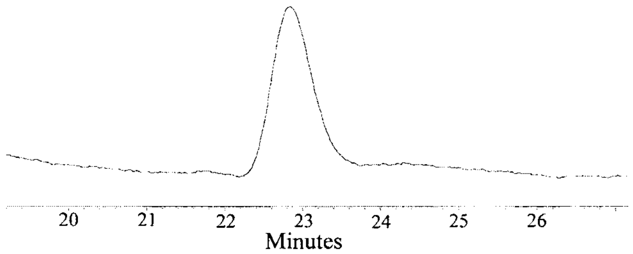
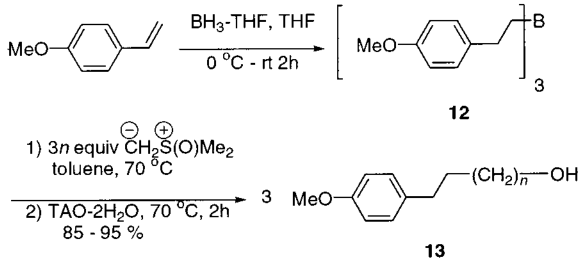


Figure 3. GPC of α-hydroxy-ω-(*p*-methoxyphenyl) polymethylene (**13**) shows a narrow, monodisperse distribution when prepared by oxidation with trimethylamine-*N*-oxide (TAO).

Scheme 5. Synthesis of Polymethylene **13** Using Tris-(4-methoxyphenylethyl) Borane (**12**)[15]



In the GPC traces (Figure 2), a smaller peak at approximately twice the molecular weight accounting for up to 5% of the total area was occasionally observed. The origin of this peak is due to trace quantities of adventitious oxygen during the oxidation step with hydrogen peroxide. The details of this reaction will be described later. Optimum conditions for oxidation were carried out with trimethylamine-*N*-oxide dihydrate (TAO) in toluene. This procedure does not require evaporation of the solvent or use of THF.[14] On occasion, discrepancies between the targeted and experimental degree of polymerization can arise if the concentration or purity of the organoborane is not known precisely. Because commercial supplies of organoboranes (i.e., Et_3B) are often contaminated with substantial amounts of boronic and borinic esters, freshly prepared solutions of trialkylboranes are preferable for use as initiators. For example, a solution of trialkylborane **12**, prepared by hydroboration of 4-vinylanisole with BH_3·THF, was used to initiate polyhomologation (Scheme 5).[15]

A representative polyhomologation consists of rapidly adding 220 μL of a 0.15 molar solution of organoborane **12** into 20 mL of 0.5 M solution of ylide **1** (300 equiv, $DP_{th} = 100$) preheated to 70 °C (Scheme 5). The reaction remained homogeneous, and ylide **1** was consumed within 10 min. The solution was cooled, 6 equiv of trimethylamine-*N*-oxide dihydrate (TAO) was added, and the solution was heated to 70 °C for 2 h (Scheme 5). The polymer was isolated by precipitation with acetonitrile followed by filtration to afford α-hydroxy-ω-(4-methoxyphenyl) polymethylene (**13**) in yields ranging from 85 to 95%. A representative GPC of polymethylene **13** (DP_{exp} = 106, Mn = 1639, PDI = 1.01) shows a narrow, monomodal distribution (Figure 3).

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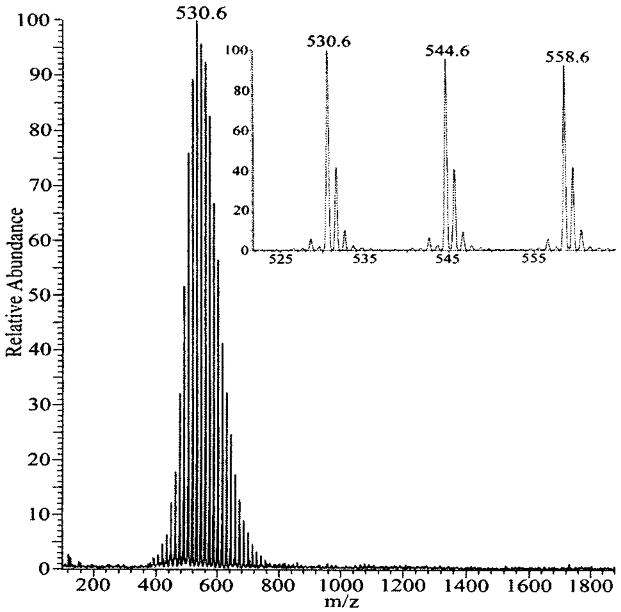

Figure 4. FDMS spectrum of α-hydroxyl-*ω*-(*p*-methoxyphenyl) polymethylene (**13**) ($M_n = 552$, $DP_{exp} = 31$, PDI = 1.01) prepared from 90 molar equiv of dimethylsulfoxonium methylide (**1**) and tris-(*p*-methoxyphenethyl) borane (**12**). Inset shows an expanded scale revealing isotope patterns with each main peak separated by 14 *m*/*e*.

Table 1. Experimental Degrees of Polymerization (DP)[a] and Polydispersities[b] of α-Hydroxyl-*ω*-(*p*-methoxyphenyl) Polymethylene **13**

		experimental DP			polydispersity	
entry	theoretical DP	NMR	FDMS	GPC	FDMS	GPC
1	23		25		1.02	
2	30	35	31	32	1.01	1.02
3	30	36	35		1.03	
4	40	45	43	39	1.03	1.01
5	40	47	44	43	1.02	1.03
6	70			75		1.01
7	140	130		149		1.03
8	228			226		1.04

[a] DP is the average number of repeat units based on the M_n. [b] Polydispersity (PDI) was calculated from M_w/M_n.

A typical field desorption mass spectrometry (FDMS) spectrum for polymethylene **13** (DP = 31, PDI = 1.01) is shown in Figure 4. The distribution consists of peaks separated by 14 amu. It is interesting to compare this spectrum with the mass spectrum of polyethylene which has peak separations of 28 amu. Mass spectrometry highlights the distinction between polymethylene and polyethylene. Polymethylene samples contain polymer chains of integral carbon numbers (*n*, *n* + 1, *n* + 2, ...), while polyethylene samples contain polymer chains of alternating numbers (*n*, *n* + 2, *n* + 4, ...).

Molecular weight analyses of α-hydroxyl-*ω*-(*p*-methoxyphenyl) polymethylene (**13**) were performed using ^{1}H NMR, FDMS, and GPC. The results are summarized in Table 1. The results establish an excellent correlation between the theoretical and observed molecular weights. Entries 2−3 and 4−5 illustrate the reproducibility of polyhomologation.

Composition of Polymethylene. The polymerization of ylide **1** by trialkyl borane followed by oxidation is expected to produce perfectly linear hydroxy-terminated polymethylene. However, a typical ^{1}H NMR spectrum of α-hydroxyl-*ω*-(*p*-methoxyphenyl) polymethylene (**13**) (Figure 5) includes a small doublet at 0.91 ppm ($J = 6.6$ Hz) corresponding to a *secondary* methyl group located on the polymer backbone. The integration of the doublet indicates one internal methyl group per 100 methylene groups (1%). In some samples, as much as 1.5% of the anomalous methyl group is observed. We attribute the origin of the internal methyl group to ethylidine incorporation that arises from a dimethylsulfoxonium ethylide impurity in ylide **1**. We have found that during synthesis of ylide **1**, small amounts of dimethylsulfoxonium ethylide (1.3%) byproduct are produced.[16] On the assumption that ethylidine and methylene incorporation occur at competitive rates,[17] a small number of ethylidine groups will be incorporated in the polymethylene chain. Ylide **1** can be recrystallized at −50 °C from toluene to produce a solution containing 0.2% dimethylsulfoxonium ethylide. Polyhomologation with purified ylide **1** produced polymethylene **13** (DP = 397), whose ^{1}H NMR spectrum (Figure 5) displays 0.2% of the anomalous signal at 0.91 ppm. The linear polymer contains fewer than two internal CH_3's per 1000 carbons.

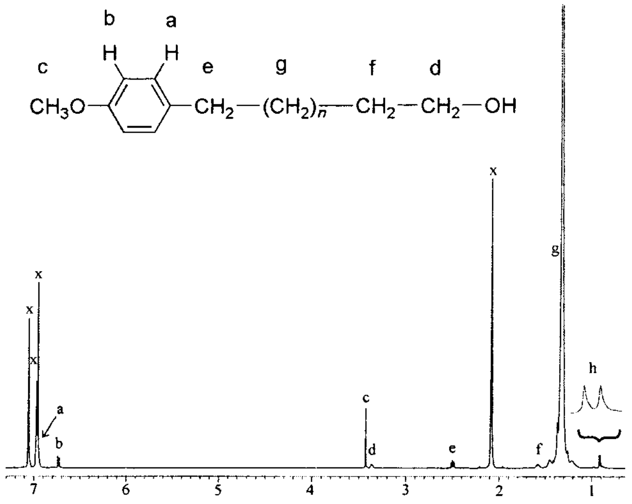

Figure 5. 500 MHz ^{1}H NMR (x: toluene-d_8) of α-hydroxyl-*ω*-(*p*-methoxyphenyl) polymethylene (**13**) ($DP_{exp} = 397$) produced from recrystallized ylide **1** and trimethylamine-*N*-oxide showing an internal methyl group (h) (0.2% methyl incorporation).

High Molecular Weight Polymethylene. When the polyhomologation reaction is carried out at 90 °C in toluene, polymethylene with a DP up to 1000 and low PDI may be produced. Higher molecular weight polymethylene precipitates during the polyhomologation under these conditions and results in broader distributions (PDI > 1.5). To overcome this problem, the polymerizations were performed in 1,2,4,5-tetrachlorobenzene (TCB)/toluene. For example, rapid injection of small amounts of triethylborane into solutions containing a large excess of ylide **1** in TCB:toluene 2:1 at 120 °C results in rapid consumption of ylide. The solution remains homogeneous throughout the reaction. Following oxidation, high molecular weight polymethylene is produced (Table 2). The control of high molecular weight is dependent upon the purity of the initiator and the ability to achieve high stoichiometric ratios

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(16) A sample of ylide **1** in toluene quenched with aqueous HCl shows 1.3% ethyldimethylsulfoxonium chloride relative to trimethylsulfoxonium chloride.

(17) Zhou, X.-Z.; Shea, K. J. *J. Am. Chem. Soc.* **2000**, *122*, 11515.

Table 2. GPC Analysis of High Molecular Weight Polymethylene

entry	$MW_t \times 10^3$	$M_n \times 10^3$	$M_w \times 10^3$	PDI
1	14.1	19.6 (15.5^b)	20.6 (17.4^b)	1.05 (1.12^b)
2	21.2	31.4 (27.0^b)	33.6 (29.4^b)	1.07 (1.09^b)
3	14.1	21.4	23.7	1.11
4	21.2	30.5	36.2	1.19
5^a	50.0	62.9	92.1	1.47
6	100	105^b	113^b	1.08^b
7^a	200	354	523	1.49

^{a} Et_3B initiator contained substantial impurities from air oxidation. ^{b} Light-scattering detector.

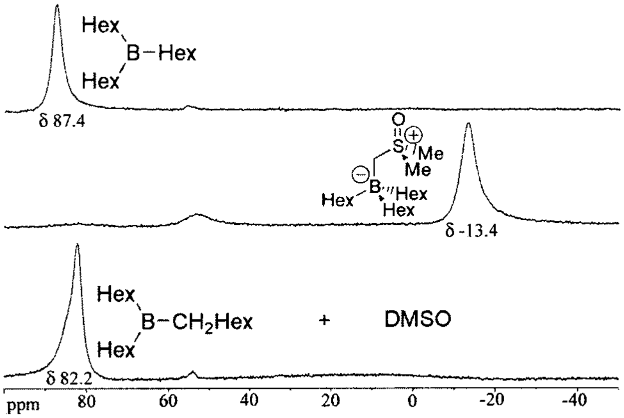
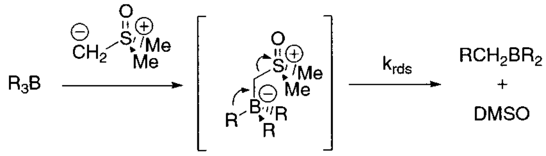


Figure 6. ^{11}B NMR of (a) tri-*n*-hexylborane (40 °C), (b) tri-*n*-hexylborane·ylide complex (−15 °C), and (c) trialkylboranes and DMSO product mixture (40 °C) in toluene. The peak at 48 ppm is a boronic acid impurity (<2%).

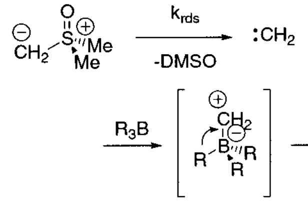
with analytical precision. For very high molecular weights, this is difficult to attain, although reproducibility and control of *relative* molecular weights are good (entries 1−4). The reproducibility is established from entries 1−3 and 2−4 which repeat molecular weight from separate experiments. However, discrepancies between theoretical and observed molecular weights are found. With commercial samples of triethylborane containing quantities of boronic and borinic esters, broader, polymodal distributions are obtained (entries 5 and 7). For polymers produced from the same batch of ylide **1** with pure triethylborane, the "theoretical" incremental increase in molecular weight of 1.5 is noted (1−2; 3−4). GPC analysis of these polymers reveals a monomodal distribution.

The efficiency of the boron center in mediating the polymerization of ylide **1** can be evaluated from the data in entry 7. The polymer arises from a tris-polymethylene borane with $M_n > 1.0 \times 10^6$. A M_n of 1.0 million for the star tris-polymethylene borane represents approximately 7.8×10^4 turnovers per boron atom. The reaction is complete in 10 min. This corresponds to a turnover frequency of 6×10^6 g of polymethylene (mol boron)$^{-1}$ h^{-1} at 120 °C. The turnover frequency for the boron catalytic center is comparable to some of the more efficient homogeneous ethylene polymerization catalysts, such as neutral anilinotropone-Ni(II) (8.8×10^6 g of polyethylene (mol catalyst)$^{-1}$ h^{-1}) (80 °C, 200 psi ethylene),[18] but less than the homogeneous metallocene catalysts such as (4,4′,5,5′-tetramethyl) bis-(fluorenylidene) (1,2-ethylidene) zirconium dichloride (2.6×10^9 g of polyethylene (mol catalyst)$^{-1}$ h^{-1}) (60 °C, 145 psi ethylene).[19]

Mechanistic Studies. By analogy with known 1,2-rearrangements of alkylboranes,[20] a plausible mechanism for the reaction involves the addition of ylide **1** to the Lewis acidic trialkylborane to form a zwitterionic complex. A subsequent 1,2-migration of one of the three-alkyl groups would afford a homologated borane. The migration is expected to occur concurrently with expulsion of dimethyl sulfoxide (DMSO) (eq 2). An alternate mechanism involving rate-limiting decomposition of ylide **1** to form carbene may also be considered. In this pathway, methylene insertion may occur through a zwitterionic complex (eq 3). Carbene intermediates have been proposed in the reaction of boranes with reactive diazoalkanes.[21] However, we have found that in the absence of Lewis acids, ylide **1** is stable to temperatures up to 120 °C. Because the homologation reaction occurs with finite rates at room temperature, it is more likely, therefore, that the addition-migration mechanism (eq 2) is operative.



(2)



(3)

^{11}B NMR was used to acquire evidence for complex formation taking advantage of a significant chemical shift difference between tricoordinate and tetracoordinate organoboron species in noncoordinating solvents. For example, the range of chemical shifts of simple trialkyl boranes is 80−90 ppm.[22] Tetraalkyl borate complexes, on the other hand, have chemical shifts in the range of −15 to −20 ppm.[22]

The ^{11}B NMR of tri-*n*-hexylborane in toluene at 40 °C exhibits a single resonance at 87.4 ppm (Figure 6). The solution was cooled to −78 °C, and an equimolar amount of ylide **1** in toluene was added. The ^{11}B NMR of the solution ($[R_3B] = 0.5$ M, $[\text{ylide}] = 0.5$ M) at −15 °C exhibits a single resonance ($\delta = -13.4$ ppm). Upon warming this mixture to 40 °C and waiting for 10 min, the ^{11}B spectrum was reacquired to reveal a single resonance at $\delta = 82.2$ ppm.

The ^{11}B NMR of the 1:1 mixture indicates complete formation of the zwitterionic intermediate. No evidence was found for uncomplexed tri-*n*-hexylborane. If one assumes that as much as 1% of the uncomplexed tri-*n*-hexylborane could have escaped detection, $K_{eq} > 2 \times 10^4$ M^{-1} for the coordination of ylide **1** to the borane. The zwitterionic complex is indefinitely stable at −15 °C. 1,2-Migration was induced by warming to 40 °C. The

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(20) Reviews: (a) Matteson, D. S. *Tetrahedron* **1998**, *54*, 10555. (b) Brown, H. C.; Ramachandran, P. V. *Pure Appl. Chem.* **1994**, *66*, 201. (c) Negishi, E.; Idacavage, M. *J. Org. React.* **1985**, *33*, 1. (d) Pelter, A. *Chem. Soc. Rev.* **1982**, *11*, 191. (e) Suzuki, A. *Acc. Chem. Res.* **1982**, *15*, 178. (f) Negishi, E. *J. Organomet. Chem.* **1976**, *108*, 281.

(21) Carbene mechanism: (a) Dorion, G.; Polchlopek, S.; Sheers, E. *Angew. Chem.* **1964**, *76*, 495. Ionic mechanism: (b) Mucha, M.; Wunderlich, B. *J. Polym. Sci.* **1974**, *12*, 1993.

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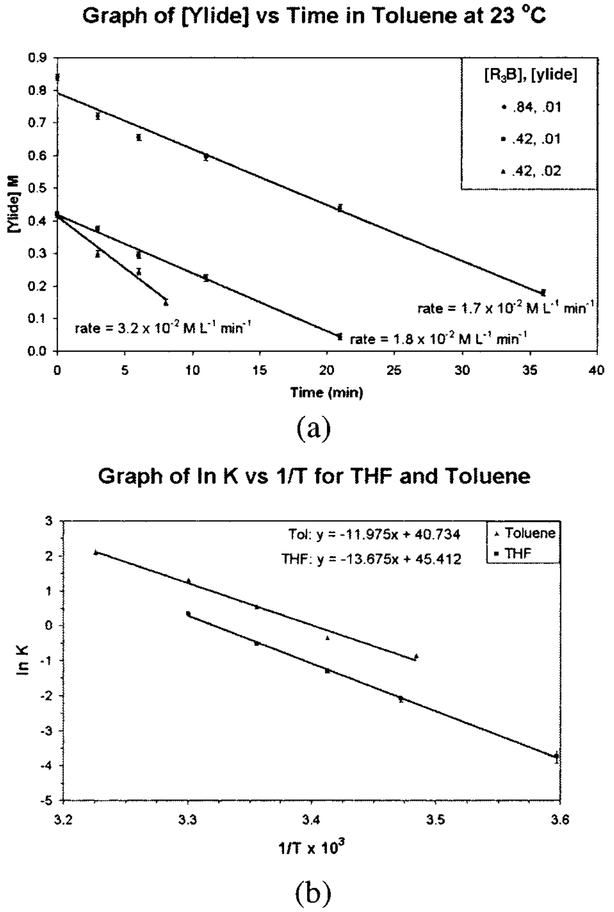


(a)

(b)

Figure 7. Kinetic study of the reaction of Et_3B with ylide **1** in toluene. (a) Graph of ylide vs time in toluene at 23 °C. (b) Graph of ln k vs $1/T$ for toluene and THF.

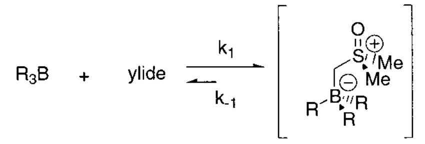
data support a preequilibrium between borane and ylide that strongly favors formation of a zwitterionic complex. This is followed by a rate-limiting 1,2-migration with concomitant expulsion of DMSO.

The chemical shift and peak shape of the homologated product differ slightly from those of tri-*n*-hexylborane. In the presence of stoichiometric quantities of coordinating solvents such as DMSO, the chemical shift of trialkyl boranes is shifted slightly upfield. Furthermore, the ^{11}B chemical shift of triethylborane in toluene with 1 equiv of DMSO exhibits a noticeable temperature dependence (1.04 ppm/°C).[23] The addition of ylide to trihexylborane and subsequent warming produces a distribution of homologated and unhomologated trialkylboranes.[11] In addition, 1 equiv of DMSO is also produced. These two factors contribute to the slight difference in chemical shift and peak shape between the starting trihexylborane (87.4 ppm) and the homologated products (82.2 ppm).

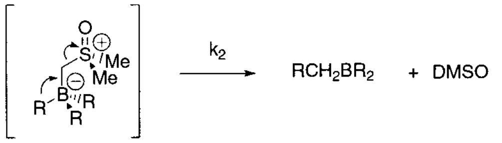
Additional support for a rate-limiting 1,2-migration step was obtained from kinetic studies. The rate of trialkylborane-catalyzed consumption of ylide **1** was monitored by hydrolyzing aliquots of the reaction mixture in water and titrating with standardized HCl to the phenolphthalein endpoint. Triethylborane was reacted with excess ylide **1** (ylide:borane > 21) in toluene or in THF. Plots of the consumption of ylide **1** versus time in toluene are linear (Figure 7). This finding indicates that accumulated DMSO does not inhibit the rate of the polyhomologation reaction. Figure 7a shows that when ylide **1** is in large excess, doubling the concentration of ylide **1** does not change the rate of consumption. However, doubling the concentration of triethylborane doubled the rate of consumption of ylide **1**. Under these pseudo first-order conditions, the reaction is first order in organoborane and zero order in ylide **1**. Similar results were obtained in THF. These results are consistent with the proposed two-step mechanism (eqs 4 and 5), with a rate-limiting 1,2-migration of the *ate* complex. The rate expression is $d[\text{product}]/dt = \text{rate} = k_2[R_3B\text{•ylide}]$. Under the reaction conditions where the ylide **1** concentration is in large excess, a rapid equilibrium between alkyl borane and ylide **1** will lie far toward the complex. Thus, the complex concentration will be close to the initial alkyl borane concentration. The rate expression can be written as rate $= k_2[R_3B]_0$, which is consistent with the kinetic study.

Table 3. Kinetic Parameters from Arrhenius Plot

parameter	THF	toluene
E_a kcal mol^{-1}	27.1 ± 1.5	23.8 ± 1.4
$\Delta H^{\ddagger}$ kcal mol^{-1}	26.5 ± 1.5	23.2 ± 1.4
$\Delta S^{\ddagger}$ cal deg^{-1} mol^{-1}	21.5 ± 5.2	12.6 ± 4.7
$\Delta G^{\ddagger}$ kcal mol^{-1} (23 °C)	20.1 ± 3.0	19.5 ± 2.8



(4)



(5)

The Arrhenius activation parameters were determined from the temperature dependence of the rate constants k over a temperature range of 15−35 °C in toluene and in THF (Figure 7b). Uncertainties in the derived activation energy parameters were evaluated using literature procedures for estimating the error propagation[24] from estimates of the uncertainty in temperature (±1 °C) and in the rate constant k. The uncertainty in k was evaluated from a regression analysis (the method of least squares).[25] The results are summarized in Table 3.

At room temperature, the free energy of activation in toluene and in THF is the same within experimental error. The narrow temperature range over which the kinetic data was acquired (20 °C) results in a significant uncertainty in the derived activation entropy. Despite this uncertainty, we believe differences in the component enthalpy and entropy of activation in the two solvents have mechanistic significance. The enthalpy of activation in THF is 3 kcal/mol higher than that in toluene, but the corresponding entropy of activation is 9 cal deg^{-1} mol^{-1} more positive. These two factors cancel at 23 °C. The origin of the effect can be understood in terms of differential solvation of

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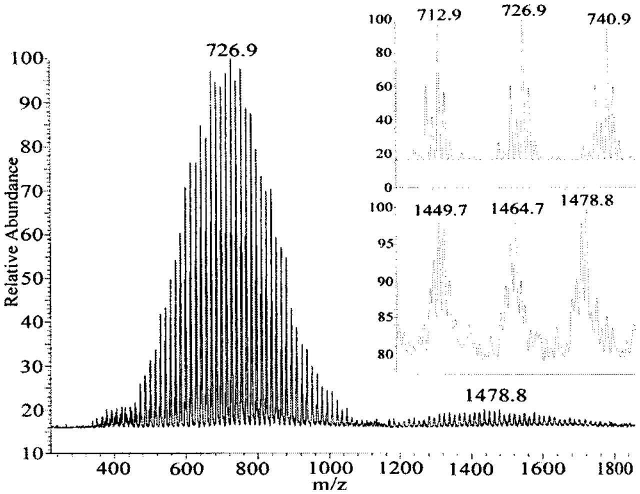

Figure 8. Field desorption mass spectrum (FDMS) of a linear α-hydroxyl-*ω*-(*p*-methoxyphenyl) polymethylene **13** when the oxidation reaction was carried out with basic hydrogen peroxide in THF. Inset shows an expansion of isotope patterns with each main peak separated by 14 *m*/*e*.

the ground and transition states by toluene and THF. The rate-limiting step involves the fragmentation of a zwitterionic complex into two neutral molecules. Charge is annihilated in the reaction. It is likely that the zwitterionic ground state elicits the greatest differential enthalpy of solvation. In THF, the highly polar ground state is more strongly solvated (stabilized) as compared to that in toluene. In the transition state, charge separation will be dissipated reducing the differential solvation enthalpy between THF and toluene. The net effect is a higher $\Delta H^{\ddagger}$ in THF. The compensating positive entropies of activation result from solvent release in the transition state. In the more strongly solvating THF, the annihilation of charge produces a greater release of strongly coordinated solvent molecules than in the weakly coordinating toluene. The net result is a more positive entropy of activation in THF than in toluene. These results are consistent with solvent effects on activation energies of related charge annihilation reactions.[26]

Reaction of Tris-polymethylene Borane with Oxygen. Routine processing of tris-polymethylene borane involved concentration of toluene prior to addition of a THF solution of basic hydrogen peroxide. These operations can expose the organoborane intermediate to oxygen. Occasionally, a second distribution amounting up to 5% of the total area is observed in the GPC traces of α-hydroxylpolymethylene (**9**) and (**10**) (Figure 2) as well as FDMS of α-hydroxyl-*ω*-(*p*-methoxyphenyl) polymethylene (**13**) (Figure 8). In the latter example, the average molecular weight ($M_n = 1453$, PDI = 1.01) of the minor distribution is approximately twice that of the major distribution ($M_n = 725$, PDI = 1.02) of α-hydroxyl-*ω*-(*p*-methoxyphenyl) polymethylene (**13**). The PDIs of both distributions are very low and could be approximated by a Poisson distribution.[27] The exact mass from high-resolution FDMS confirms that the major distribution is composed of α-hydroxyl-*ω*-(*p*-methoxyphenyl) polymethylene (**13**). Figure 9a shows an expansion of the spectrum at *m*/*z* 726 corresponding to the molecular ion $[M]^+$ for $C_{50}H_{94}O_2$ at *m*/*z* 726. The $[M + 1]^+$ and $[M + 2]^+$ peaks have relative intensities (57% and 16%, respectively) as expected on the basis of the natural isotopic abundance (calculated = 100:57.1:16.6). In addition, there are significant peaks for $[M - 2]^+$ and $[M - 4]^+$ ions with relative intensities of 43% and 11% at *m*/*z* 724 and 722, respectively. The FDMS spectra of polyethylene commonly produce $[M - 2]^+$ ions from loss of H_2 with intensities ranging from 10 to 20% relative to the $[M]^+$ ion dependent on the applied voltages and the molecular weight.[28] The $[M - 4]^+$ ion has not been observed previously. We propose that the anomalous intensities of the $[M - 2]^+$ ion arise from molecular ions from secondary products aldehyde-terminated **15** and methyl-terminated polymethylene **16** (Scheme 6). The $[M - 4]^+$ ion arises from loss of H_2 from either **15** or **16**.

From the high-resolution FMDS (Figure 9b), the mass-doubled materials can be assigned to di(*ω*-(*p*-methoxyphenyl) polymethylene) ether (**17**) or a mixture of **17** and α,*ω*-di(*p*-methoxyphenyl) polymethylene (**18**) (Scheme 6). The isotope pattern is consistent with the polymethylene ether **17** and displays an $[M - 2]^+$ ion which could arise from α,*ω*-di(*p*-methoxyphenyl) polymethylene (**18**) or the loss of H_2 from polymer **17**.

Support for the presence of these products and their assignments can be found in the corresponding ^1H NMR (Figure 10). The overlapping triplet at 0.89 ppm ($J = 6.0$ Hz) is consistent with a methyl-terminated polymethylene **16**. The doublet at 0.91 ppm ($J = 6.6$ Hz) is from the internal methyl group. The triplet at 9.39 ppm ($J = 1.8$ Hz) and doublet of triplets at 1.91 ppm ($J = 7.4$, 1.8 Hz) correspond to the aldehyde proton and the adjacent methylene group in the aldehyde-terminated polymethylene **15**, respectively. No evidence for olefin protons could be found. The overlapping small peak at 3.33 ppm may be tentatively assigned to the methylene group adjacent to the etheral oxygen in the polymethylene ether **17**.

We propose that the origin of these minor products arises from reaction of oxygen with tris-polymethylene borane. Following consumption of ylide **1**, the intermediate tris-polymethylene borane **14** can react with trace quantities of adventitious oxygen to produce a mixture of carbon and oxygen centered radicals **19**, **20** (Scheme 6).[29] Radicals generated in this way have been used as a source of macromonomers which can initiate free radical polymerization of other vinyl monomers for the synthesis of copolymers.[30] In the absence of added monomers and at low O_2 concentration, the radicals **19** and **20** can undergo dimerization to produce a mixture of mass-doubled polymethylene **17** and **18**. Alternatively, radicals may undergo disproportionation to form **15** and **16**. The pathway to produce olefin-terminated polymethylene is not observed and may not be favored since the C=O bond is stronger than the C=C bond.

Additional support for the explanation of the O_2 induced radical byproducts can be found from the fact that the mass-doubled distribution is eliminated when the intermediate tris-

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(26) Reichardt, C. *Solvents and Solvent Effects in Organic Chemistry*, 2nd ed.; VCH Verlagsgesellschaft: Weinheim, Fed. Rep. Ger., 1990; pp 136–147.

(27) The calculated polydispersity of the minor distribution was 1.01. The theoretical relationship between the major and the minor distribution is related to the reaction mechanism that links them. The relationship is considered in the Appendix. Both major and minor distributions are closely approximated by a Poisson distribution (see Appendix).

(28) (a) Heine, C. E.; Geddes, M. M. *Org. Mass Spectrom.* **1994**, *29*, 277. (b) Evans, W. J.; DeCoster, D. M.; Greaves, J. *J. Am. Soc. Mass Spectrom.* **1996**, *7*, 1070.

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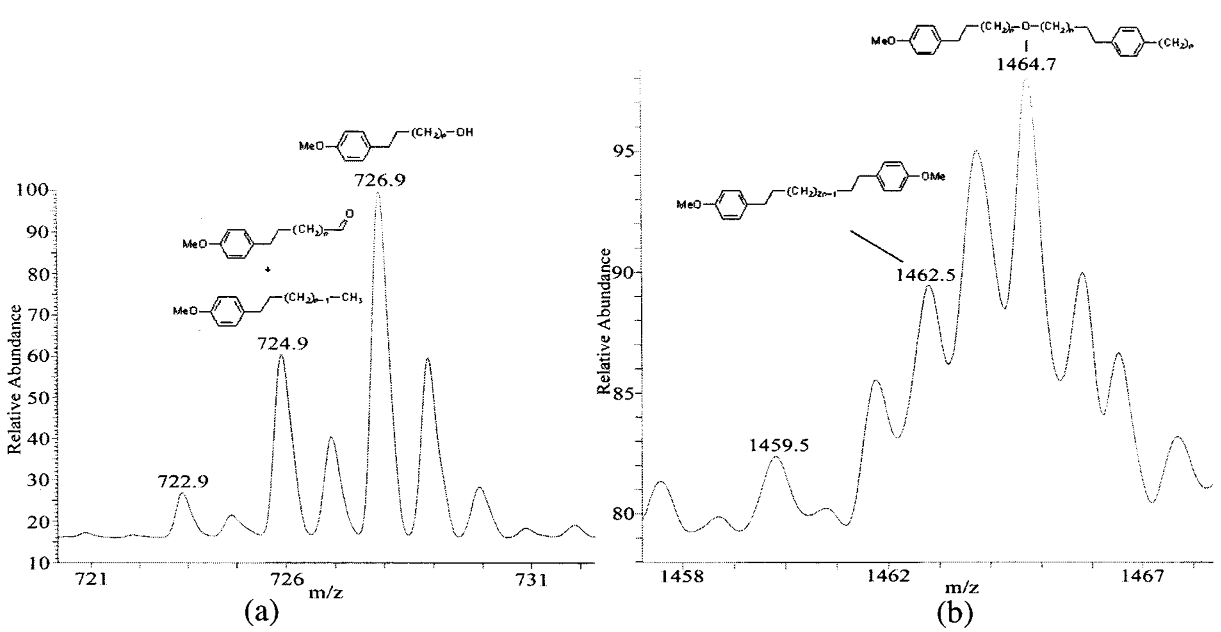

Figure 9. (a) Expansion for the molecular ion peak for $C_{50}H_{94}O_2$ of polymethylene **13** at *m*/*z* 726 showing a mixture of three polymers: hydroxyl-terminated **13** (DP = 41), methyl-terminated **16** (DP = 42), and aldehyde-terminated **15** (DP = 41) polymethylene. (b) Expansion of the molecular ion peak for $C_{102}H_{190}O_3$ in the mass-doubled region showing a possible mixture of two polymers: α,*ω*-di(*p*-methoxyphenyl) polymethylene ether (**17**) (DP = 84) and di(*ω*-(*p*-methoxyphenyl) polymethylene) (**18**) (DP = 85).

polymethylene borane is reacted directly with trimethylamine-*N*-oxide dihydrate (TAO) after the ylide **1** is consumed. The sample handling in the latter case does not require evaporation of the solvent and introduction of THF, mitigating exposure of the tris-organoborane to oxygen. Another possible source of these byproducts is the alkali oxidation with hydrogen peroxide. Alkane impurities from hydrolytic cleavage[31] of boranes have been reported as byproducts from oxidation with neutral hydrogen peroxide.[32] The TAO oxidation protocol avoids both of these potential problems.

Conclusion

Triorganoboranes mediate the polymerization of dimethylsulfoxonium methylide **1**. One mole of DMSO is produced for each mole of ylide consumed. The product of the polymerization is a 3-arm star polymethylene borane. Oxidative cleavage of the tris-star-polymethylene produces a hydroxyl-terminated polymethylene with molecular weights up to 500 000 D. Typical polydispersities are <1.1. The reaction involves association of ylide **1** and trialkylborane to form a zwitterionic complex. The complex may be directly observed at <−15 °C ($K_{eq} > 2 \times 10^4$). The activation energy E_a for rate-limiting 1,2-migration was determined in THF (27.1 kcal/mol) and toluene (23.8 kcal/mol). The reported boranes initiate the polymerization of ylide **1** with a turnover frequency of 6×10^6 g of polymethylene (mol boron)$^{-1}$ h^{-1} at 120 °C.

Experimental Section

General Methods. Toluene and hexanes were distilled over CaH_2 under N_2. THF was passed through an activated alumina column under Ar. All other chemicals were used as received without further purification. Solutions of borane dimethyl sulfide complex and triethylborane were obtained from Aldrich. The triethylborane solutions indicated varying amounts of impurities. The borane dimethyl sulfide was pure by NMR and titration.[33] ^{1}H and ^{13}C NMR spectra were obtained using either Bruker Omega-500 MHz or General Electric GN-500 MHz spectrometers at 500 and 125 MHz, respectively, and calibrated with residual undeuterated toluene-d_8 and $CDCl_3$. The ^{11}B NMR at 160 MHz was calibrated with an external standard of $BF_3 \cdot OEt_2$. GPC data were obtained using a Waters 150C Plus GPC using *O*-xylene as the eluent at 100 °C at 1 mL/min. Samples for chromatography were prepared as 0.5−0.6% solutions in *O*-xylene. Four Ultrastyragel (5 *μ*m particle size) were used in series: (500 Å × 2), (100 Å × 2). The GPC calibration curve was made with polyethylene standards from Polymer Laboratories and from Scientific Polymer Products. High molecular weight polymethylene samples were analyzed at Exxon-Mobil. The FDMS spectra were obtained under conditions previously described.[28b] Elemental analyses were performed at Atlanta Microlab, Inc. IR was obtained on an Analect RFX-40 FTIR spectrophotometer. Melting points were obtained on a Thomas-Hoover Unimelt apparatus and are uncorrected.

All hydroboration and polyhomologations were performed in flame-dried glassware under an atmosphere of N_2. The borane initiators were handled under N_2. The intermediate tris-organoborane polymers are air sensitive and were oxidized by briefly removing the septum to add the solid TAO, and continuing the reaction under N_2. Oxidation with H_2O_2/NaOH involved incautious exclusion of air during manipulations.

Dimethylsulfoxonium Chloride (7). A biphasic mixture of CH_2Cl_2 (325 mL) and H_2O (440 mL) containing trimethylsulfoxonium iodide **6** (42.8 g, 194.5 mmol, 1.0 equiv) and benzyltributylammonium chloride (65.1 g, 208.7 mmol, 1.1 equiv) was vigorously stirred in a flask protected from light for 17 h. The aqueous layer was separated, washed with CH_2Cl_2 (1 × 60 mL), and evaporated in vacuo. The white solid was recrystallized from 95:5 MeOH:toluene, filtered, ground to a fine powder, and dried in a vacuum oven (50 °C, 15 mmHg) for

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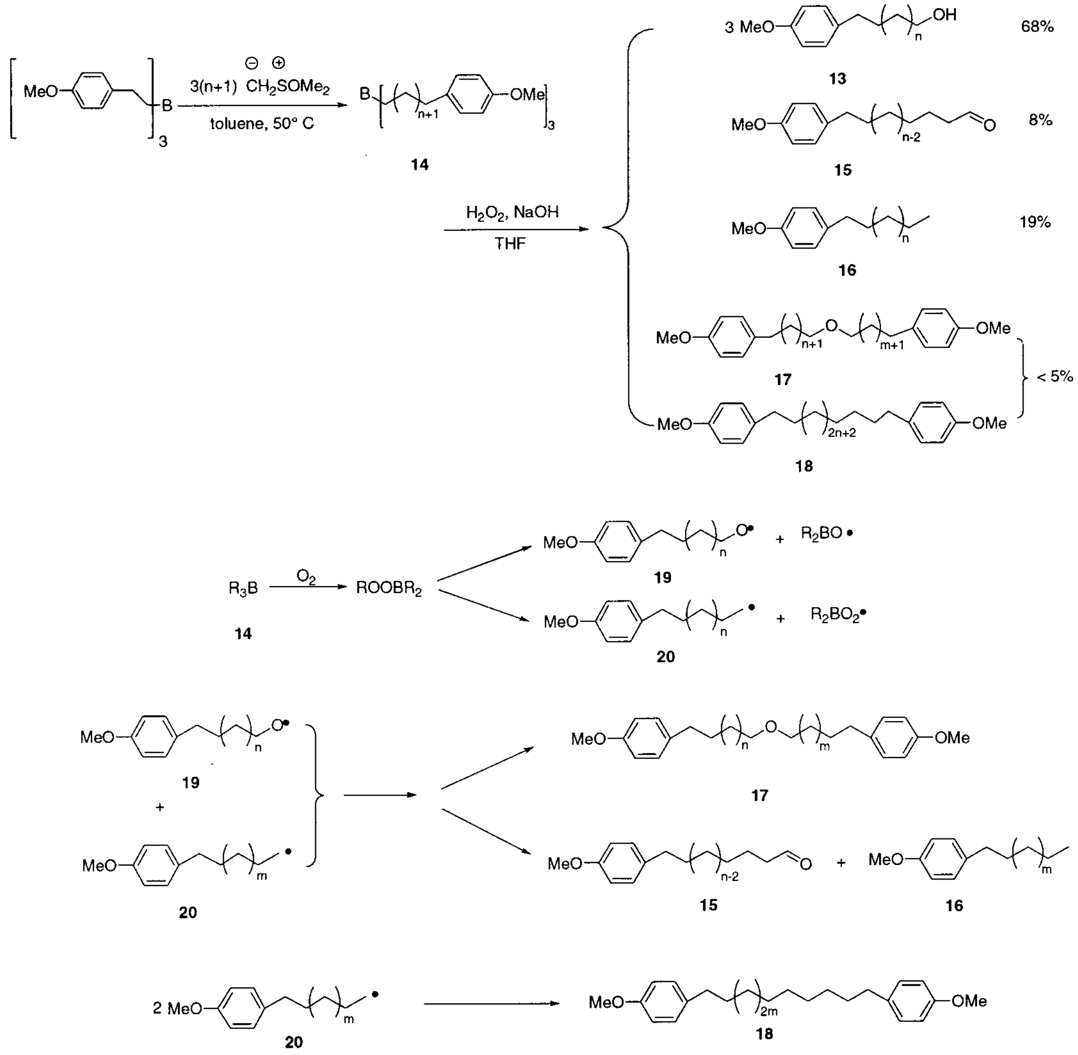
Scheme 6. Possible Products from the Reaction of Oxygen with Tris-polymethylene Borane **14**



22 h to yield a white powder (24.6 g, 98.4% yield). mp 220.2−221.8 °C (lit.[34] mp 222−223). IR (KBr): ν_{max} 2968.2, 2885.3, 1411.7, 1342.0, 1316.2, 1232.9, 1047.4, 961.8, 765.8 cm^{-1}. ^{1}H NMR (500 MHz, DMSO-d_6): δ 3.91 (s). ^{13}C NMR (125 MHz, DMSO-d_6): δ 38.8.

Dimethylsulfoxonium Methylide (1). Sodium hydride (60% dispersion in oil, 3.40 g, 84.3 mmol) was washed with hexanes (3 × 20 mL) under nitrogen. Final traces of solvent were removed in vacuo. Powdered and dry trimethylsulfoxonium chloride (**7**) (8.34 g, 64.8 mmol) and toluene (75 mL) were transferred to the flask. The heterogeneous reaction mixture was heated at reflux in anhydrous THF or toluene until evolution of H_2 had stopped (2−4 h). The contents were cooled to room temperature and filtered under nitrogen through predried Celite 545 to afford a colorless solution of ylide **1** (0.76 M in toluene, 88.0% yield). The solution was stored at −20 °C. An aliquot of the solution (0.2 mL) was added to H_2O (5 mL) and titrated with standardized HCl before use. Solutions of ylide **1** in toluene can be recrystallized under nitrogen by cooling the solution to −50 °C, decanting the supernatant from the colorless needles with a syringe, and adding an equal volume of toluene.

Optimized Conditions for Polyhomologation. α-Hydroxypolymethylene. Borane•SMe$_2$ (1.0 M in CH_2Cl_2, 0.235 mL, 0.235 mmol) was rapidly added via syringe to a solution of ylide **1** (0.68 M in toluene, 103.5 mL, 70.4 mmol) at 75 °C under N_2. After 10 min, a drop of the reaction mixture was added to H_2O (3 mL) containing phenolphthalein and indicated ylide **1** had been consumed. The reaction was cooled to room temperature, the septum to the reaction flask was removed to add trimethylamine-*N*-oxide dihydrate (156 mg, 1.4 mmol), capped, and heated at 60 °C for 2 h under N_2. The reaction was cooled to room temperature and precipitated with CH_3CN (200 mL). Filtration, washing with CH_3CN (20 mL), acetone (20 mL), and hexane (20 mL), and drying afforded a white solid (1.00 g, 100% yield). ^{1}H NMR (500 MHz, toluene-d_8, 50 °C): 3.37 (t, J = 6.4 Hz, 2H), 1.35 (s, 203H), 0.93 (m, 13H). GPC M_n = 1437, M_w = 1477, PDI = 1.028. Anal. Calcd for $C_{100}H_{202}O$: C, 84.55; H, 14.33. Found: C, 84.57; H, 14.34.

Tris-(4-methoxyphenylethyl) Borane (12). A solution of BH_3•THF (1.0 M in THF, 0.56 mL) was added over 5 min to a solution of 4-vinylanisole (0.25 mL, 1.88 mmol) in THF (2.4 mL) at 0 °C. The reaction was allowed to warm to room temperature over 2 h. The initiator (0.19 M in THF) was used immediately without further purification. Oxidation of a small aliquot of the solution with H_2O_2 and NaOH indicated a 94:6 ratio of expected regioisomers.

α-Hydroxy-ω-(4-Methoxyphenyl) Polymethylene (13). Tris-(4-methoxyphenylethyl) borane (**12**) (0.24 M in THF, 0.75 mL, 0.15 mmol) was rapidly injected via syringe under N_2 into a solution of ylide **1** (0.58 M in toluene, 31 mL, 18 mmol) at 55 °C. After 7 min a drop of the reaction was added to water containing phenolphthalein. The neutral solution indicated ylide **1** was consumed. The reaction was cooled to room temperature, toluene was removed in vacuo, THF (5 mL), NaOH (6 M, 0.2 mL, 1.2 mmol), and H_2O_2 (30%, 0.2 mL, 1.2 mmol) were

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(34) Braendstroem, A.; Lamm, B. *Acta Chem. Scand., Ser. B* **1974**, *28*, 590.

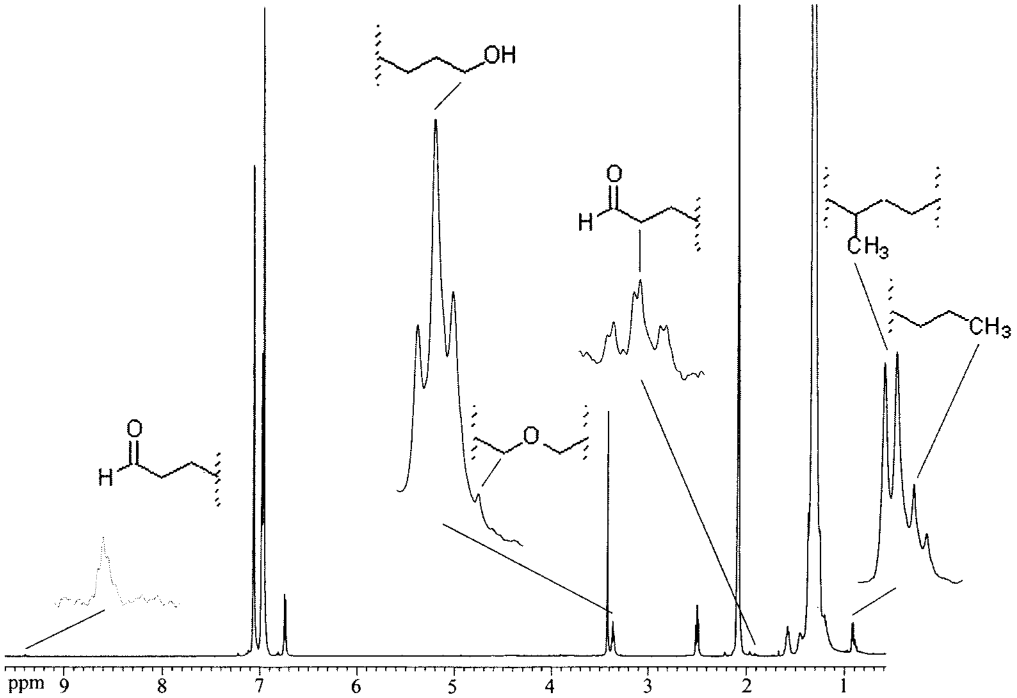

Figure 10. 500 MHz ^{1}H NMR of α-hydroxyl-*ω*-(*p*-methoxyphenyl) polymethylene (**13**) produced by oxidation with H_2O_2 and NaOH.

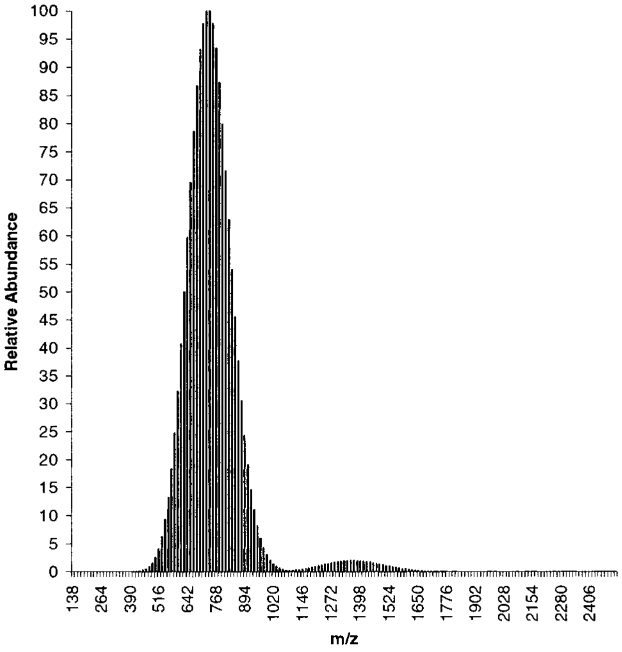

Figure 11. Simulation of distribution of α-hydroxyl-*ω*-(*p*-methoxyphenyl) polymethylene **13** with 2% of dimer.

added at 0 °C, and stirred at room temperature for 4 h in a flask vented with a syringe needle. Addition of CH_3CN (40 mL), filtration of the precipitate, and drying in vacuo afforded a white solid (290 mg, 92% yield). ^{1}H NMR (500 MHz, toluene-d_8, 50 °C): δ 6.76 (d, 2H, $J = 8.4$ Hz), 3.40 (s, 3H), 3.35 (t, 2H, $J = 5.8$ Hz), 2.49 (t, 2H, $J = 7.6$ Hz), 1.40−1.25 (s, 100H), 0.91 (m, 3H), $DP_{exp} = 50$. ^{13}C NMR (125 MHz, toluene-d_8, 50 °C): δ 129.4, 114.5, 62.9, 55.0, 37.8, 35.6, 33.5, 32.1, 30.7, 30.5, 30.3, 30.2, 30.1, 27.7. IR (KBr): υ_{max} 3448, 2919, 2850 cm^{-1}. FDMS analysis: $M_p = 768.6$, PDI = 1.02. GPC: $M_n = 687$, $M_w = 703$, PDI = 1.01. Anal. Calcd for $C_{64}H_{122}O_2$: C, 83.33; H, 13.32. Found: C, 83.63; H, 13.34.

α-Hydroxypolymethylene (8) (High Molecular Weight). Ylide **1** (0.66 M in toluene, 10 mL, 6.6 mmol) was added to a melt of degassed 1,2,4,5-tetrachlorobenzene (20 g) at 55 °C. The temperature was raised to 125 °C. Triethylborane (0.01 M in hexanes, 31 μL, 0.31 μmol) was rapidly added via syringe, and the reaction was stirred under N_2. After 10 min, a drop of the reaction mixture was added to water containing phenolphthalein and indicated that ylide **1** had been consumed. Sodium hydroxide (1 M, 1 mL, 5 mmol) and H_2O_2 (30%, 1 mL, 5 mmol) were added, and the solution was stirred for 2 h. The solution was concentrated in vacuo (25 mmHg) at 150 °C, cooled to room temperature, and CH_3CN (50 mL) was added. The precipitate was filtered and dried in vacuo to afford a white solid (87 mg, 89% yield). ^{1}H NMR (500 MHz, toluene-d_8, 80 °C): δ 3.35 (t, $J = 6.4$ Hz), 1.40−1.25 (m), 0.91 (d, $J = 6.6$ Hz). ^{13}C NMR (125 MHz, toluene-d_8, 80 °C): δ 30.1. IR (KBr): ν_{max} 3480, 2919, 2850 cm^{-1}. GPC analysis: $M_w = 104 \times 10^3$, $M_n = 100 \times 10^3$, PDI = 1.04. $T_m = 126.8$ °C. Anal. Calcd for $C_{5500}H_{11000}O$: C, 85.60; H, 14.38. Found: C, 85.68; H, 14.47.

Low-Temperature ^{11}B NMR Studies. Tri-*n*-hexylborane. Borane·SMe_2 (2.0 M in CH_2Cl_2, 10.3 mL, 20.6 mmol) was added over 5 min to a solution of 1-hexene (8.0 mL, 63.6 mmol) in CH_2Cl_2 (20 mL) at 0 °C. The solution was allowed to warm to room temperature over 2 h. The mixture was purified by removing all volatiles in vacuo (0.01 mmHg) at 50 °C for 2 h. The material was kept in a glovebox and used immediately. ^{1}H (500 MHz, C_6D_6): δ 1.49 (m, 2H), 1.33 (m, 6H), 1.26 (m, 2H), 0.93 (t, $J = 7.0$ Hz, 3H). ^{13}C (125 MHz, C_6D_6): δ 33.6, 32.7, 29.1 (br), 25.3, 23.5, 14.8. ^{11}B (160 MHz, C_6D_6, 40 °C): δ 87.4. IR (NaCl): ν_{max} 2940, 1458, 1344 cm^{-1}.

Tri-*n*-hexylborane·ylide Complex. An NMR tube containing tri-*n*-hexylborane (94 mg, 0.35 mmol) was cooled to −78 °C. A solution of ylide **1** (0.605 M in toluene, 0.58 mL, 0.35 mmol) at −20 °C was added. The mixture was shaken and kept below −40 °C. ^{11}B NMR (160 MHz, toluene, −15 °C): δ −13.4. The mixture was warmed for 10 min at 40 °C. ^{11}B NMR (160 MHz, toluene, 40 °C): δ 82.2.

Kinetics. General for THF or Toluene. A solution of ylide **1** (50 mL) in either THF or toluene was stirred at the desired temperature (±0.1 °C) in a water bath. A measured amount of Et_3B (1 M in THF) was rapidly injected, and the reaction was stirred under N_2. Aliquots

(5.00 mL) were withdrawn at different time intervals, added to H_2O (50 mL), and titrated with 0.1 N HCl to the phenolphthalein endpoint.

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Appendix

The distribution function of polymer chains in a living polymerization is given by a Poisson distribution.[35] The polyhomologation of ylide **1** with R_3B produces a polymer distribution that closely approaches this function. The reaction of this product with O_2 will give a distribution of radicals. What is the expected distribution of dimers? The following analysis was performed to establish the nature of the new distribution. The distribution of the polymeric radicals generated from the reaction is a Poisson distribution (eq 6)

$$X_i = \frac{\nu^{i-1} e^{-\nu}}{(i-1)!} \tag{6}$$

where X_i is the number fraction of *i*-mer radical (denoted by R_i), and ν is the number average chain length.

To obtain an expression of X_{i+j} we need to write down all the ways in which $(i + j)$-mer (denoted by $P_{(i+j)}$) can be formed and then sum the number fractions of these processes. The possible reactions that form $(i + j)$-mer are shown in eqs 7−12.

$$R_{i+j-1} + R_1 \rightarrow P_{i+j} \tag{7}$$

$$R_{i+j-2} + R_2 \rightarrow P_{i+j} \tag{8}$$

$$. \; . \; . \; . \; . \; . \; . \; . \; . \; . \; . \; . \; . \tag{9}$$

$$R_{i+j-m} + R_m \rightarrow P_{i+j} \tag{10}$$

$$. \; . \; . \; . \; . \; . \; . \; . \; . \; . \; . \; . \; . \tag{11}$$

$$R_1 + R_{i+j-1} \rightarrow P_{i+j} \tag{12}$$

The number fraction of $(i + j)$-mer can then be expressed by eq 13.[36]

$$X_{i+j} = \sum_{m=1}^{i+\mathrm{j}-1} \frac{\nu^{i+j-m-1} e^{-\nu}}{(i+j-m-1)!} * \frac{\nu^{m-1} e^{-\nu}}{(m-1)!} = \sum_{m=1}^{i+j-1} C_{i+j-2}^{m-1} * \frac{\nu^{i+j-2} e^{-2\nu}}{(i+j-2)!} = \frac{(2\nu)^{i+j-2} e^{-2\nu}}{(i+j-2)!} \tag{13}$$

The form of the expression X_{i+j} is still a Poisson function. This indicates that the random combination of a Poisson distribution of radicals should produce a Poisson distribution of dimers at twice the mass with a very narrow molecular weight distribution with PDI values close to unity (PDI = 1.01 with DP = 85). A plot of the calculated distributions with 2% of dimers is shown in Figure 11.

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