Synthesis of Linear α-Olefins via Polyhomologation

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ABSTRACT: Linear α-olefins (LAOs) of controlled molecular weight and low PDI were synthesized in high yield by the polyhomologation reaction of dimethylsulfoxonium methylide (**1**) with triallylborane (**2**). Following polymerization, propionic acid or trimethylamine *N*-oxide dihydrate (TAO) was used to afford α-vinyl-*ω*-methyl or α-vinyl-*ω*-hydroxy end-functionalized polymethylene, respectively. Controllable molecular weights up to 13 kDa were obtained by varying the initial monomer/catalyst ratio, and the resultant polymers had very narrow polydispersities (PDI < 1.08). Although polymer yields were generally high, quantities of oxidized side products were observed in α-vinyl-*ω*-methyl samples; however, these oxidized side products could be removed for samples of low molecular weights ($C_n \leq 36$).

Introduction

Linear α-olefins (LAO) in the range of C_6−C_{20} represent an important starting material for many commercial polymers, including detergents, lubricants, and comonomers for ethylene polymerizations to form LDPE and VLDPE.[1] A variety of transition metal catalysts (Ni, Zr, Cr) have been used to synthesize LAOs through the oligomerization of ethylene. An alternative synthesis of LAOs with controlled molecular weight distributions remains in high demand. Studies in our laboratory have concentrated on developing a new approach to synthesizing LAOs using a living polymerization of dimethylsulfoxonium methylide (**1**) by trialkylboranes. In this reaction, the alkyl groups of the trialkylboranes undergo repetitive 1,2-migrations with ylide monomers to build the carbon backbone of the developing polymethylene polymers one carbon at a time. This process of repetitive 1,2-migration, or homologation has been termed polyhomologation.[2] The polyhomologation reaction has demonstrated its versatility in the construction of novel materials ranging from star polymers[3] to copolymers of polymethylene and poly(dimethylsiloxane)s[4] to the commercially important commodity copolymer poly(ethylene-*b*-styrene).[5] By developing and combining new monomer sources, the polyhomologation reaction has also yielded a route to a material with the same chemical composition as an ethylene−propylene copolymer.[6]

For synthesis of controlled molecular weight distributions of linear α-olefins, we have focused on utilizing the polyhomologation reaction with a suitable trialkylborane initiator and installing a terminal vinyl group either following or prior to polyhomologation. Prior efforts in pursuit of the former concentrated on the polyhomologation of triethylborane with dimethylsulfoxonium methylide (**1**)[7] followed by heating (250 °C) under high vacuum (0.05 mmHg) in an attempt to effect retro-hydroboration to install a terminal vinyl group. These efforts were not successful. While the retro-hydroboration is expected to be thermodynamically favored at high temperature, the process, even at these elevated temperatures, is kinetically prohibitive.

An alternative approach using triallylborane (**2**) as initiator was explored. Following polyhomologation of triallyborane (**2**), reductive cleavage of the B−C bond by treatment of the oligomeric and polymeric triorganoboranes (**3**) with propionic acid could provide conditions for the protolysis of the carbon−boron bonds of **3**. As an alternative to propionic acid, we also investigated milder methods for the protolysis of polymeric triorganoboranes **3** using 2-hydroxypyridine[8] (Scheme 1).

Results and Discussion

Synthesis and Properties of Triallylborane. Triallylborane (**2**) was prepared as described by the method of Zakharkin and Stanko.[9] Allylaluminum sesquibromide, formed by the reaction of allylbromide with solid aluminum granules, was reacted with boron trifluoride etherate to give triallylborane in 60% yield after two distillations (Scheme 2).

In contrast to most alkylboranes, triallylborane displays high reactivity toward water, alcohols, and other nucleophiles in reactions that often result in cleavage of the C−B bond.[10] Since ylide **1** has been shown to react with electron-deficient olefins,[11] its mode of reaction with triallylborane was in question. The application of triallylborane for the synthesis of functionalized, linear α-olefins by the polyhomologation reaction would represent a novel use for this versatile reagent.

Polyhomologation of Triallylborane. In the synthesis of LAOs, triallylborane (**2**) serves as an initiator while dimethylsulfoxonium methylide (**1**) is the methylene monomer source. One equivalent of DMSO is expelled for each equivalent of ylide **1** consumed. Random insertion into all three carbon−boron bonds results in the formation of a polymeric organoborane (**3**). The living nature of the polyhomologation reaction allows control of the average length of each growing chain of **3**.[12] Providing each branch grows randomly, subsequent oxidation of **3** provides α-vinyl-*ω*-hydroxypolymethylene (**5**) (Scheme 3).

Toluene solutions of ylide **1** were preheated to 80 °C and treated with an aliquot of a toluene solution of **2**. The ylide was rapidly consumed (5 min). TAO[13] was added directly to the solution to affect oxidation under reflux conditions. TAO was used in preference to basic hydrogen peroxide to affect oxidation because the latter results in a small amount (1−2%) of polymethylene with twice the average molecular weight of a given sample due to radical coupling.[14] Removal of solvents followed by filtering and washing of the polymeric solids with

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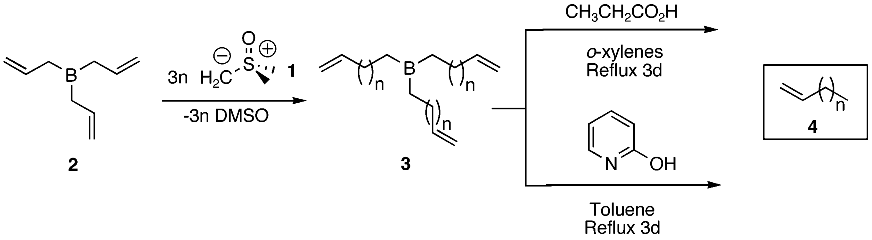
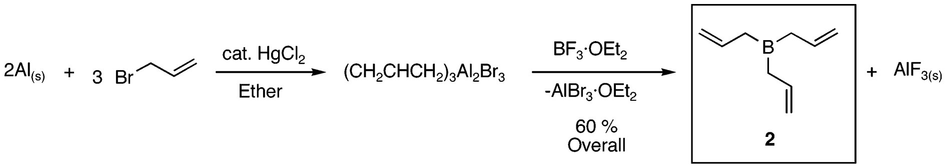
Scheme 1



Scheme 2



Scheme 3

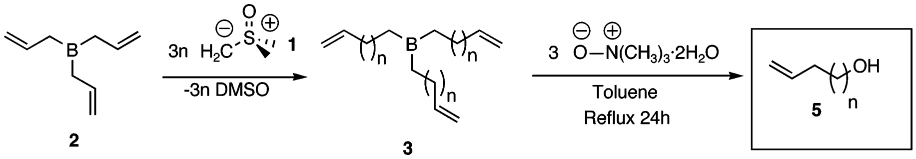


Table 1. GPC and ^1H NMR Data of α-Vinyl-ω-hydroxypolymethylene 5 (Scheme 3)

trial	DP^a (calcd)	$M_n{}^b$ (g/mol)	DP^b	DP^c ^1H NMR	PDI
1	20			38	
2	40	498	31	55	1.12
3	54	712	47	72	1.05
4	108	1396	96	133	1.03
5	400	6690	473		1.05
6	800	13202	937		1.06

[a] The DP refers to *n* (Scheme 6). [b] Data refer to GPC in *o*-xylenes at 100 °C calibrated with linear polyethylene standards. [c] Data refer to ^1H NMR end-group analysis (i.e., the ratio of the terminal hydroxymethylene proton to the broad polymethylene peak of **5**).

methanol, water, and hexanes gave near-quantitative crude yields of polymer **5**. Samples were further purified by reprecipitation in toluene/acetonitrile to afford an opaque white polymer in 88−94% yield. The structural assignment of the polymer **5** is as follows.

The ^1H NMR spectra of **5** (C_6D_6, 77 °C) have features consistent with α-vinyl-ω-hydroxypolymethylene (**5**). Diagnostics include resonances at 5.78 ppm (ddt, J = 17.0, 10.4, 6.6 Hz, 1H), corresponding to the vinylic methine proton of **5**. Also, resonances at 5.02 ppm (dd, J = 17.1, 1.8 Hz, 1H) and at 4.95 ppm (dd, J = 10.2, 1 Hz, 1H) correspond to the terminal vinylmethylene protons of **5**. A triplet at 3.39 ppm (t, J = 6.5 Hz, 2H) and a quartet at 2.01 ppm (q, J = 6.9, 2H) correspond to the hydroxymethylene and methylene protons of the allylic carbon of **5**, respectively. A broad signal at 1.35 ppm corresponds to the polymethylene protons of **5**. The doublet at 0.93 ppm arises from the incorporation of 1−2% ethylidene groups in the polymethylene backbone arising from dimethylsulfoxonium ethylide, formed as a minor product in the synthesis of ylide **1**[13] (Figure 1).

Table 2. GPC and ^1H NMR Data of Vinylpolymethylene (4) Produced by Scheme 2

trial	DP^a (calcd)	$M_n{}^b$ (g/mol)	DP^b	DP^c ^1H NMR	PDI
1	64	1038	70	65	1.04
2	127	2426	169	183	1.05

[a] The DP refers to *n* (Scheme 2). [b] Data refer to GPC in *o*-xylenes at 100 °C calibrated with linear polyethylene standards. [c] Data refer to ^1H NMR end-group analysis (i.e., the ratio of the terminal hydroxymethylene proton to the broad polymethylene peak of **4**).

The degree of polymerization (DP) was established by GPC and ^1H NMR end-group analysis (Table 1). Reactions were run with initial ratios of ylide:triallylborane of 60, 120, 162, 324, 1200, and 2400. If all three allyl groups of triallylborane undergo homologation, these reactions should produce α-vinyl-ω-hydroxypolymethylene (**5**) with n = 20, 40, 54, 108, 400, and 800, respectively. In all cases, the DP by GPC and ^1H NMR end-group analysis correlated closely to the calculated values. The data are summarized in Table 1.

The GPC traces for all samples in Table 1 were monomodal. Both the relative and absolute correlations between the DP calculated for trials 3 and 4 (54 and 108) and the DP determined by GPC (47 and 96) demonstrate molecular weight control for the synthesis of **5**. Further, the low PDI for all trials is indicative of a living polymerization.

Reactions of **3** with two proton sources, propionic acid[15] and 2-hydroxypyridine,[8] were explored (Scheme 1). For protolysis by propionic acid, reactions were run with initial ratios of ylide:triallylborane of 192 and 381. It was anticipated that this reaction would yield α-vinyl-ω-methyl-polymethylene (**4**) with n = 64 and 127, respectively. GPC data and ^1H NMR end-group analysis for these experiments are presented in Table 2.

For trials 1 and 2 in Table 2, after ylide consumption, the toluene and DMSO were removed in vacuo, and the product was dissolved in a 1:1 *o*-xylene:propionic acid (20 equiv) solution and refluxed under nitrogen for 3 days.

For protolysis by 2-hydoxypyridine, reactions were run with initial ratios of ylide:triallylborane of 138 and 276. Following protolysis of the carbon−boron bond of **3**, these reactions were expected to yield α-vinyl-ω-methylpolymethylene (**4**) with n = 46 and 92, respectively. GPC data and ^1H NMR end-group analysis for these experiments are presented in Table 3.

For trials 1 and 2 in Table 3, after ylide consumption, 2-hydroxypyridine (16 equiv) was added to the reaction

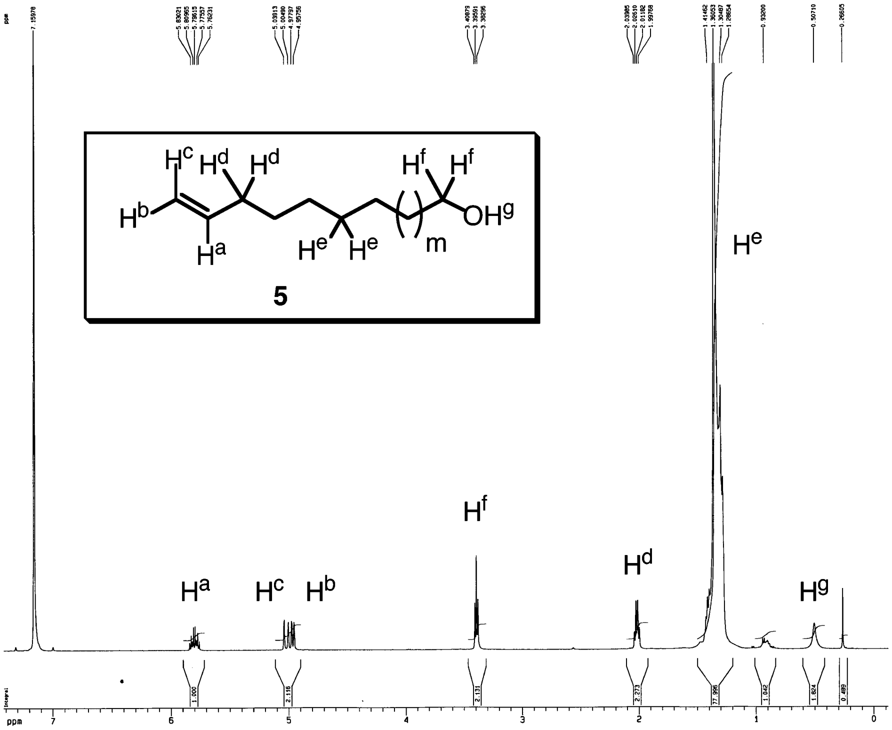


Figure 1. Representative ^1H NMR spectrum of the polymer **5** (C_6D_6, 77 °C). The spectrum shown corresponds to trial 1 in Table 1. The broad singlet at 0.5 ppm has been assigned to the hydroxyl proton of the end group.

Table 3. GPC and ^1H NMR Data of Vinylpolymethylene (4) Produced by Scheme 3

trial	DP[a] (calcd)	M_n[b] (g/mol)	DP[b]	DP[c] ^1H NMR	PDI
1	46	665	43	61	1.08
2	92	1282	87	113	1.03

[a] The DP refers to n (Scheme 3). [b] Data refer to GPC in *o*-xylenes at 100 °C calibrated with linear polyethylene standards. [c] Data refer to ^1H NMR end-group analysis (i.e., the ratio of the terminal hydroxymethylene proton to the broad polymethylene peak of **4**).

solution, and the reaction was refluxed for 3 days. Solvents were removed in vacuo, and the recovered polymeric product **4** for each trial was redissolved in toluene and precipitated with acetonitrile to afford 80−86% yield of **4** after filtering and washing with water, methanol, and hexanes. The ^1H NMR spectra of the polymeric samples of **4** produced by all reactions in Table 2 and Table 3 indicate that approximately 20−30% of the polymer chains have some terminal oxygen functionality. Chemical shifts of approximately 3.5 ppm in the ^1H NMR of these oligomers are consistent with terminal hydroxyl (or peroxy) groups. An earlier study of the reaction products of tris(polymethylene)borane with oxygen suggests the oxygenated biproducts are comprised of ω-hydroxy- and peroxy-terminated polymethylene.[14] The oxygen-terminated chains may arise from oxidation of the polymeric alkylborane (**3**) by adventitious oxygen over the 3 days required for the reaction. Comparison of the theoretical DP with the DP determined by GPC indicates the absolute molecular weights can be controlled within a narrow range. While perfectly oxygen-free polymeric samples of α-vinyl-ω-methylpolymethylene (**4**) are frequently desired to serve as comonomers with ethylene with oxygen-sensitive polyethylene metallocene catalysts for the synthesis of novel comb polymers, there have been reports of ethylene polymerization $Ni(COD)_2$ catalysts that tolerate oxygen-containing functional groups in α-vinyl-ω-functional-olefin comonomers.[16]

Oligomeric α-Vinyl-ω-methylpolymethylene in the C_9−C_{36} Range. To evaluate the effectiveness of the protolysis of the carbon boron bonds of oligomer (**3**), a reaction with a ratio of ylide:triallylborane of 36 was conducted and followed by treatment with propionic acid (Scheme 2). After the ylide was consumed, the toluene and DMSO were removed in vacuo, and the crude oligomeric **3** was refluxed in neat propionic acid (360 equiv, 3 days). The short-chain oligomeric α-vinyl-ω-methylpolymethylene (**4**) was extracted with hexanes and ether, and the organic layers were washed with saturated potassium carbonate, dried over sodium sulfate, and removed in vacuo to give an 86% yield of **4** after purification by chromatography (SiO_2, hexanes). This reaction should yield oligomeric linear α-vinyl-ω-methylpolymethylene centered approximately at C_{15}. The GC chromatograph of this reaction is shown in Figure 2.

Each peak in the spectrum has a mass separation of 14.0 *m*/*z*. The peak at the retention time of 4.57 min has a mass (EI) of 140.2 *m*/*z* and corresponds to 1-decene. The PDI of the distribution shown in Figure 3 is 1.09. The calculated DP from the M_n of the distribution corresponds to the C_{20} linear α-olefin. Importantly, there was no evidence for any oxygen-terminated linear α-olefins in the GC spectrum or the ^1H NMR spectra of oligomer **4** (Figure 3). The absence of oxygen-terminated linear α-olefins in this oligomeric sample of **4** may be attributed to the isolation of the oligomers by extraction and their purification by chromatography. The ^1H NMR spectra of **4** have features consistent with the proposed assignment of an α-vinyl-ω-methylpolymethylene structure.

While the center of the distribution is slightly higher than that calculated on the basis of the stoichiometry, the GC chromatograph and the ^1H NMR spectra of **4**

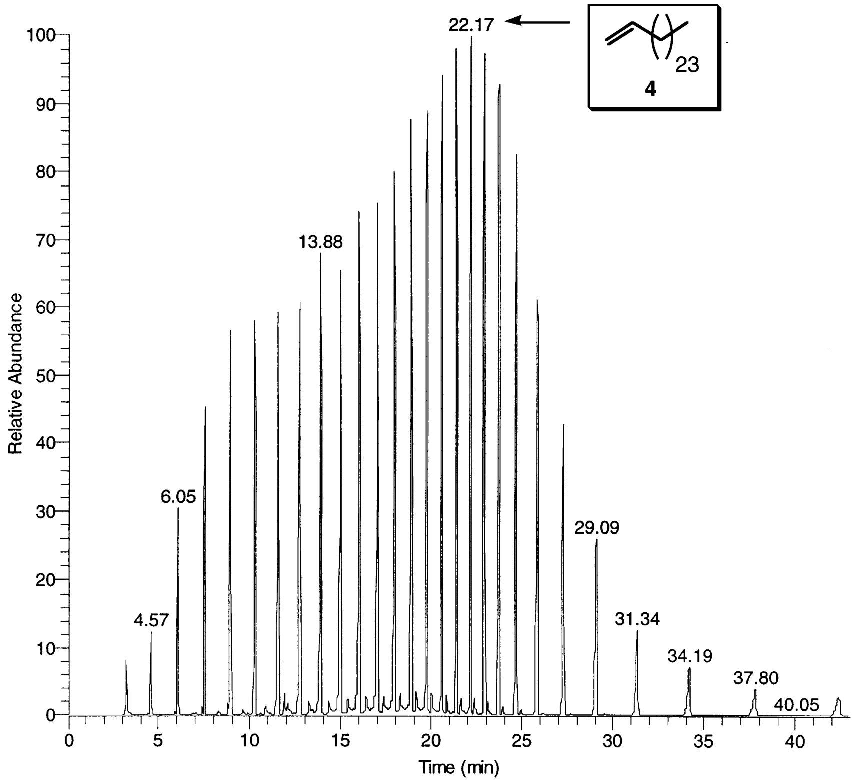


Figure 2. GCMS chromatograph of oligomeric linear α-vinyl-ω-methyl-polymethylene (**4**) produced by the polyhomologation reaction. The distribution ranges from C_9 to C_{36}. The peak at the retention time of 22.17 min has a mass (EI) of 364.4 *m/z* and corresponds to the C_{26} linear α-vinyl-ω-methylpolymethylene (**4**). The baseline distribution of peaks offset from the main distribution correspond by mass to isomeric, α-olefin chains that incorporate 1−2% ethylidene groups.[13]

demonstrate that triallylborane can be used to access linear α-vinyl-ω-methylpolymethylene (**4**) in the C_9−C_{36} range by polyhomologation in high yield.

Conclusions

Triallylborane (**2**) was employed in the polyhomologation reaction to synthesize α-vinyl-ω-functionalized-polymethylene of controlled molecular weight and low PDIs. Following polyhomologation of triallylborane with oxidation by TAO provides access to polymeric (C_{40}−C_{800}) samples of α-vinyl-ω-hydroxypolymethylene (**5**) of controlled molecular weight and low PDI. Following the polyhomologation of triallylborane with reduction by propionic acid or 2-hydroxypyridine yields impure polymeric (C_{40}−C_{180}) α-vinyl-ω-methylpolymethylene (**4**) contaminated with 20−30% of an oxygen-terminated impurity. However, oligomeric (C_9−C_{36}) α-vinyl-ω-methylpolymethylene (**4**) can be isolated in high yield by the polyhomologation of triallylborane followed by reduction with refluxing propionic acid and purification by chromatography.

Experimental Section

General Information. All ^{1}H NMR spectra were acquired at 400 or 500 MHz. Chemical shifts (δ) are listed in ppm against internal references. Coupling constants (*J*) are reported in hertz. All ^{13}C NMR spectra were acquired at 125.8 MHz. Chemical shifts (δ) are listed in ppm against solvent carbon peaks as an internal reference. All ^{11}B NMR spectra were acquired at 237 MHz. All chemical shifts (δ) are listed in ppm against boron trifluoride etherate as an external reference. All GPC was conducted on a high-temperature gel permeation chromatograph using xylenes as the mobile phase. Pure hydrocarbons and narrow molecular weight polyethylene were used as calibration standards. The synthesis and standardization of toluene solutions of dimethylsulfoxonium methylide (**1**) have been described elsewhere.[14]

Triallylborane (2). The method of Zakharkin and coworkers was followed to synthesize **2**.[9] To a flame-dried 250 mL round-bottom flask sealed with rubber septum and equipped with a magnetic stir bar, reflux condenser, and thermometer was transferred solid aluminum granules (12.03 g, 446 mmol) and $HgCl_2$(s) (88 mg, 0.32 mmol). Dry, N_2-purged diethyl ether (60 mL) was added, and the solution was stirred and heated to 35 °C. Allyl bromide (52.1 mL, 602 mmol) was added dropwise under a nitrogen atmosphere. Care must be taken to add the allyl bromide slowly, since the reaction with aluminum is exothermic. The reaction mixture was stirred at reflux in an oil bath set at 67 °C for 3 h. The reaction mixture was then transferred via syringe into a septum-sealed flame-dried 250 mL round-bottom flask containing $BF_3{\cdot}Et_2O$ (20.0 mL, 142 mmol) under nitrogen. This solution was refluxed at 70 °C for 3 h. The ether was removed by short-path distillation under nitrogen. The residue was then distilled under vacuum (20 mmHg) with a short-path distillation head at a head temperature of 65 °C to give crude triallylborane as a clear, colorless liquid (17.00 g, 78%). ^{11}B NMR (237 MHz, $CDCl_3$) of this distillate showed a major peak, δ 80.7 (br s) 83%, and minor peaks at δ 50.6 (br s) 11%, and δ 32.0 (br s) 6%. The peak at δ 80.7 (br s) has been assigned to triallylborane. On the basis of chemical shift, the peak at δ 50.6 has been tentatively assigned to a borinic ester of some type, most likely the product of triallylborane's reaction with oxygen. A second vacuum distillation (20 mmHg) yielded pure triallylborane as a clear, colorless liquid (13.07 g, 60%). ^{1}H NMR (500 MHz, $CDCl_3$) δ: 2.2 (br s, 6H), 4.9 (br s, 6H), 5.89−5.98 (p, $J = 10.6$, 3H). ^{13}C NMR (125.8 MHz, $CDCl_3$) δ: 134.8, 114.7 (br s), 34.4 (br s). ^{11}B NMR (237 MHz, $CDCl_3$) δ: 80.6 (br s). IR (neat): 3076, 2999, 2973, 2914, 1807, 1635, 1420, 1370, 1270, 1170, 993, 900 cm^{-1}.

α-Vinyl-ω-methylpolymethylene (4). *General Method.* Toluene solutions of ylide **1** were preheated to 80 °C and treated with an aliquot of a toluene solution of triallylborane

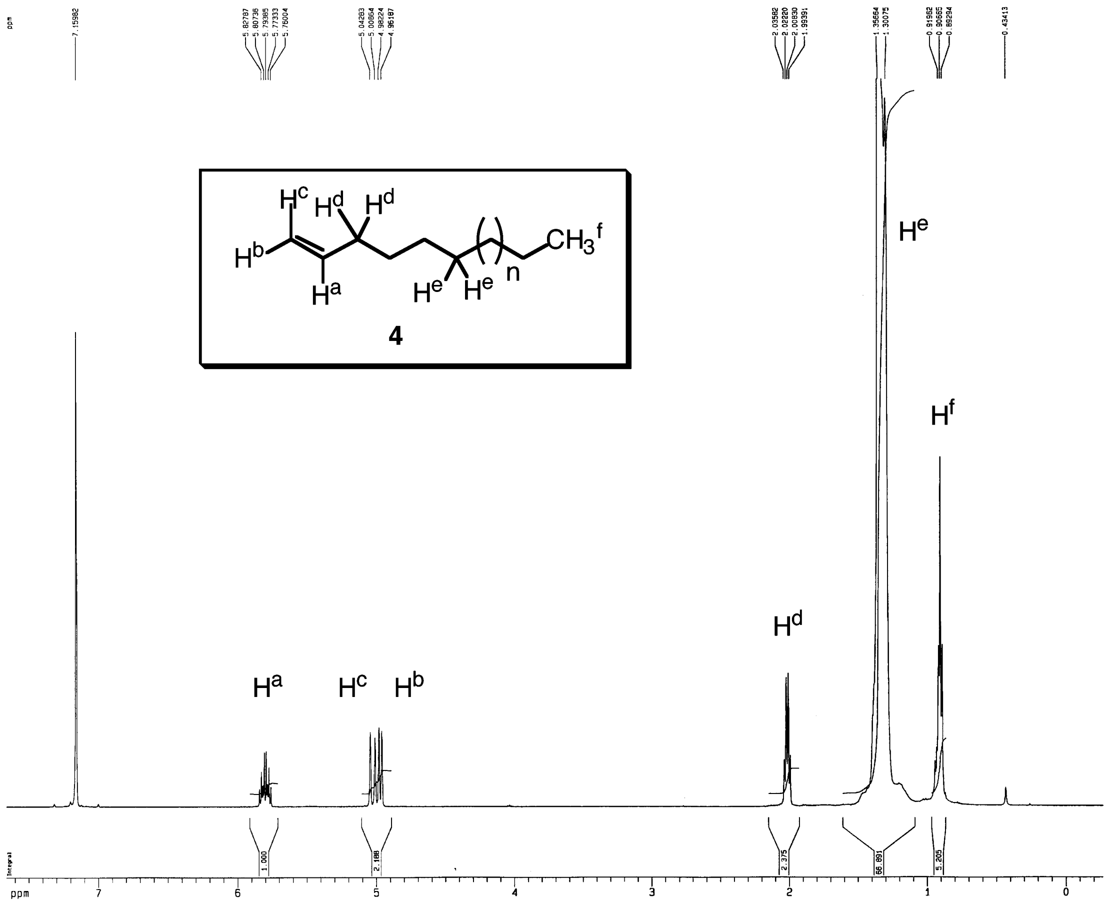


Figure 3. ^{1}H NMR spectrum of the oligomer **4** (C_6D_6, 67 °C). The integration of the terminal methyl group (H^f) is high due to the incorporation of 1−2% ethylidene groups.[13]

(**2**). The ylide was rapidly consumed (5 min), solvents were removed in vacuo, and a 1:1 *o*-xylenes:propionic acid (20 equiv) was added and the reaction was refluxed for 3 days. Removal of solvents followed by filtering and washing of the polymeric solids with methanol, water, and hexanes gave near-quantitative crude yields of polymeric **4**. Purification by reprecipitation in toluene/acetonitrile afforded a purified white polymer **4** in yields of 80−90% (spectrocopic data for trial 1 of Table 2). ^{1}H NMR (500 MHz, toluene-d_6, 78 °C) δ: 5.78 (ddt, J = 17.0, 10.3, 6.7 Hz, 1H), 5.00 (dd, J = 17.2, 1.7 Hz, 1H), 4.94 (dd, J = 9.6, 1.0 Hz, 1H), 3.36 (m, 0.3 H), 1.98 (q, J = 6.9, 2H), 1.35 (m, 130H), 0.91 (m, 3H). ^{13}C NMR (125.8 MHz, toluene-d_6, 78 °C) δ: 30.1. IR: 3447 (br), 2918, 1473, 1463, 730, 719 cm^{-1}.

α-Vinyl-ω-hydroxypolymethylene (5). *General Method.* Toluene solutions of ylide **1** were preheated to 80 °C and treated with an aliquot of a toluene solution of triallylborane (**2**). The ylide was rapidly consumed (5 min), and trimethylamine-*N*-oxide dihydrate (3.1 equiv) was added to affect oxidation under reflux conditions. Removal of solvents followed by filtering and washing of the polymeric solids with methanol, water, and hexanes gave near-quantitative crude yields of polymeric **5**. Purification by reprecipitation in toluene/acetonitrile afforded a purified white polymer **5** in yields of 80−90% (spectrocopic data for trial 1 of Table 1). ^{1}H NMR (500 MHz, toluene-d_6, 78 °C) δ: 5.78 (ddt, J = 17.0, 10.4, 6.6 Hz, 1H), 5.00 (dd, J = 17.2, 1.8 Hz, 1H), 4.94 (dd, J = 10.2, 1 Hz, 1H), 3.36 (m, J = 6.5 Hz, 2H), 2.00 (q, J = 6.9, 2H), 1.35 (m, 77H), 0.91 (m 1H), 0.49 (br s, 2H). ^{13}C NMR (125.8 MHz, toluene-d_6, 78 °C) δ: 30.1. IR: 3319 (br), 2918, 1463, 909, 729 cm^{-1}.

α-Vinyl-ω-methylpolymethylene (4). *Oligomeric Method.* A toluene solution of ylide **1** (52.2 mmol) was preheated to 80 °C and treated with an aliquot of triallylborane (**2**) (1.5 mmol). The ylide was rapidly consumed (15 min), solvents were removed in vacuo, and propionic acid (536 mmol) was added and the reaction was refluxed for 3 days. The crude oligomeric **4** was extracted with hexanes and ether, and the organic layers were washed with saturated potassium carbonate, dried over sodium sulfate, and removed in vacuo to give an 86% yield of oligomeric **4** after purification by chromatography (SiO_2, hexanes). ^{1}H NMR (500 MHz, C_6D_6, 77 °C) δ: 5.80 (ddt, J = 17.0, 10.3, 6.6 Hz, 1H), 5.02 (dd, J = 17.1, 1.7 Hz, 1H), 4.97 (d, J = 10.2 Hz, 1H), 2.01 (q, J = 7.2, 2H), 1.35 (m, 66H), 0.91 (t, J = 6.9, 5H). ^{13}C NMR (125.8 MHz, C_6D_6, 77 °C) δ: 139.6, 114.7, 34.5, 32.7, 30.5, 30.4, 30.3, 30.2, 30.1, 29.8, 29.7, 23.4, 14.5. IR: 2918, 2850, 1464, 992, 910, 730, 720 cm^{-1}.

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