

M solution in THF) at 40 °C led to consumption of the ylide within 10 min.⁶ During the course of the reaction, the solution became cloudy. The solution was concentrated then treated with basic peroxide (NaOH/H₂O, THF, H₂O). The resulting white waxy solid (>95% yield) was dissolved in hot toluene and reprecipitated with CH₃CN. Spectral properties (NMR, IR) of the product were consistent with a hydroxy-terminated long-chain alkane.⁷

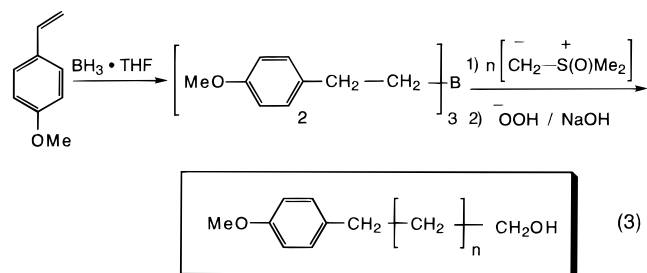
The polyhomologated samples were analyzed by both field desorption mass spectrometry (FDMS) and gel permeation chromatography (GPC) as well as by NMR end group analysis. The average molecular weights by NMR were consistent with those calculated from the ratio of alkylborane to ylide assuming equal probability of migration of all three alkyl groups. However, GPC analysis and FDMS indicated somewhat broad, polymodal distributions of oligomer chain lengths. The rapid consumption of ylide and high mass balance of straight chain alcohol is consistent with repetitive homologation reactions resulting eventually in formation of oligomeric polymethylene.⁸ We speculated that the broad distribution of polymer chain lengths could be due to competing precipitation of the propagating polymer chains during polyhomologation, since hydrocarbon chains beyond 30 carbons are insoluble in most organic solvents, including THF, at room temperature.

Polymethylene is soluble in toluene at elevated temperatures. When a toluene solution of ylide **1**, preheated to 70–80 °C, was treated with triethylborane, the ylide was rapidly consumed (5 min) and the solution remained homogeneous. After concentration and oxidative workup, a quantitative yield of hydroxyl terminated polymethylene was obtained.

The average molecular weight was found to be very close to the initial ratio of 1:3 (ylide/trialkylborane). In three experiments with ratios of 50, 117, and 232, the experimentally determined \overline{DP} (GPC, polyethylene standards) were 48, 108, and 231 (Table 1). The degree of molecular weight control is consistent with a *living polyhomologation reaction* with no termination step.

Living polymerizations have characteristically low polydispersities (PDIs).⁹ The oligomeric products from the polyhomologation reactions exhibited PDIs that ranged from 1.04 to 1.17 (Table 1).

Polyhomologation of alkylboranes is amenable to the syntheses of telechelic polymethylene.¹⁰ This is illustrated by the preparation of α -(*p*-methoxyphenyl)- ω -hydroxypolymethylene (eq 3). The initiator, tris-(*p*-methoxyphenyl)ethylborane, **2**, prepared by hydroboration of *p*-vinylanisole with BH₃·THF, was added via syringe to a preheated toluene solution of ylide.

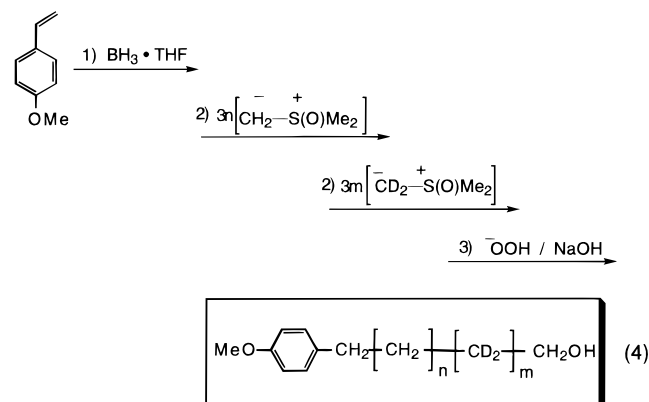


After consumption of ylide (5 min), concentration, and oxidation (THF, H₂O₂, NaOH), a quantitative yield of α -(*p*-methoxyphenyl)- ω -hydroxy polymethylene was obtained. For samples prepared with an initial (ylide/alkylborane)^(1/3) ratio of 58:1, the average DP calculated by FDMS is 66.¹¹ The

(6) Progress was monitored by removing aliquots, quenching with H₂O and titrating the base produced with standard HCl. Ylide solutions of **1** in the absence of borane show no reaction after 6 h at 80 °C. S. Y. Lee, unpublished results.

polydispersity (M_w/M_n) of this sample was of 1.02 using GPC (polyethylene standards) and 1.01 using FDMS (see Figure 1).

Living polyhomologations are also amenable to synthesis of block copolymers. An illustration is the synthesis of α -hydroxy- ω -(*p*-methoxyphenyl)polymethylene-*co*-polyperdeuteriomethylene (eq 4). The copolymer was prepared by the addition of



tris-(*p*-methoxyphenyl)ethylborane (**2**) to a toluene solution of ylide **1**. Following consumption of ylide, a solution of perdeuterio **1** was added. After consumption of the second batch of ylide, the tris-polyhomologated alkylborane was oxidized to the terminal alcohol.

FDMS analysis reveals distribution of molecular ions at *m/e* consistent with a copolymer of α -hydroxy- ω -(*p*-methoxyphenyl)polymethylene containing (CH₂)_n(CD₂)_m units¹² where 3*n* and 3*m* represent the equivalents of protio and perdeuterio ylide **1** added.

Polyhomologation is a general technique for extending organoboranes by a predetermined number of methylene groups. The reaction permits control of functionality at both ends of the polymer chain. Its living nature permits introduction of polymethylene grafts to a number of organic polymers. The extension of this technology to include grafted polymethylene surfaces, block copolymers, substituted polymethylenes, and molecules of unusual topology will be reported in time.

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Supporting Information Available: Experimental details (3 pages). See any current masthead page for ordering and Internet access instructions.

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(7) For previous work on the synthesis of terminally functionalized polyethylene oligomers, see: (a) Bergbreiter, D. E.; Blanton, J. R.; Chandran, R.; Hein, M. D.; Huang, K. J.; Treadwell, D. R.; and Walker, S. A. *J. Polym. Sci.: Part A, Polym. Chem.* **1989**, *27*, 4205. (b) Bergbreiter, D. E. *Prog. Polym. Sci.* **1994**, *19*, 529.

(8) The intermediates in these polymerizations are organoboron polymers. Their characterization and properties are currently being explored. For the synthesis of related organoboron-containing polymers, see: (a) Chujo, Y.; Tomita, I.; Hashiguchi, Y.; Tanigawa, H.; Ihara, E.; Saegusa, T. *Macromolecules* **1991**, *24*, 234. (b) Chung, T. C.; Janvikul, W.; Bernard, R.; Jiang, G. J. *Macromolecules* **1994**, *27*, 26. (c) Chung, T. C.; Rhuhrig, D. J. *Polym. Sci.: Part A, Polym. Chem.* **1993**, *31*, 2759. (d) Ramakrishnam, S. *Macromolecules* **1991**, *24*, 3753.

(9) For reviews of living polymerizations, see: (a) Webster, O. W. *Science* **1991**, *251*, 887. (b) Aida, T. *Prog. Polym. Sci.* **1994**, *19*, 469.

(10) (a) Jerome, R.; Henriouille-Granville, M.; Boutevin, B.; Robin, J. J. *Prog. Polym. Sci.* **1991**, *16*, 837. (b) Tezuka, Y. *Prog. Polym. Sci.* **1992**, *17*, 471.

(11) The calculation assumes quantitative formation of alkylborane. (12) FDMS revealed the polymer sample contained *p*-MeOPh(CH₂)_n-(CD₂)_m-OH block copolymer contaminated with small amounts of *p*-MeOPh-(CH₂)_n-OH which presumably arises from quenching of the oligomeric polymethylene upon addition of the deuterated ylide.