Communications to the Editor

Polyhomologation. A Living Polymethylene **Synthesis**

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The linear hydrocarbon polymethylene differs from polyethylene in that the polymer chain is built up one carbon at a time. Polymethylene has been synthesized by the catalyzed polymerization of diazomethane.¹ We report a new polymerization reaction, polyhomologation, for the synthesis of polymethylene. The reaction utilizes methodology developed for the homologation of organoboranes. Application of this chemistry to polymer synthesis is unprecedented.

Tufarello and co-workers developed a procedure for homologation of alkylboranes by reaction with ylides such as dimethylsulfoxonium methylide (1, eq 1).² After reaction with an



equivalent of ylide, the alkylborane was oxidized (H₂O₂, NaOH, H₂O) to the terminal alcohol. The reaction produced product mixtures that contained mono- and bishomologated alcohols as well as nonhomologated product. Subsequent refinements of this homologation reaction and related chain extension strategies of organoboranes comprise valuable additions to synthetic methodology.^{3,4}

The homologation reaction in eq 1 involves initial attack of ylide on the alkylborane. The borate complex undergoes a 1,2migration of the alkyl group to produce the homologated alkylborane and a molecule of dimethyl sulfoxide (eq 2).



^{(1) (}a) Imoto, M.; Nakaya, T. J. Macromol. Sci.-Rev. Macromol. Chem. 1972, C7, 1. (b) Mucha, M.; Wunderlich, B. J. Polym Sci. Polym. Phys. 1974, 12, 1993.

Table 1. Molecular Weight and Polydispersity of Oligomeric Hydroxyl-Terminated Polymethylene

Et ₃ B	1) n [CH ₂ —S(O)Me ₂]	
	2) OOH / NaOH	

polymer	DP (calcd from feed ratio)	$\overline{\text{DP}}$ (GPC) ^a	\overline{M}_{n} (GPC)	PDI (GPC)
J	50	48	727	1.04
$Et(CH_2)_nCH_2OH$	117	108	1563	1.05
	232	231	3287	1.17

^a Analysis performed on a Waters 150 C+ system with o-xylene as the mobile phase (26 mL/min) at 105 °C. Pure hydrocarbons and narrow molecular weight polyethylene standards were used for calibration.



Figure 1. FDMS of telechelic polymethylene. The field desorption technique does not result in polymer fragmentation. The spacing between peaks (14 emu) is characteristic of polymethylene in contrast to polyethylene which exhibit spacings of 28 emu. The average molecular weight corresponds to MeOPh(CH₂)₆₉CH₂OH. The M_w/M_n = 1.01.

The product of this migration, a homologated alkylborane, can react with additional ylide. The minor amounts of bishomologated product noted as a side product in the original report of this reaction² are consistent with this mechanism.

In the absence of competing nucleophiles, the reaction, in principle, may be repeated many times. To evaluate if repetitive homologation would be amenable to the synthesis of polymethylene, we examined the reaction of simple alkylboranes with a large excess of ylide. It was observed that the addition of triethylborane (0.47 mmol, 1 M solution in THF) to a THF solution of dimethyl sulfoxonium methylide⁵ (106 mmol, 0.8

 ^{(2) (}a) Tufariello, J. J.; Lee, L. T. C. J. Am. Chem. Soc. 1966, 88, 4757.
 (b) Tufariello, J. J.; Wojtkowski, P.; Lee, L. T. C. J. Chem. Soc., Chem. Commun. 1967, 505. (c) Tufariello, J. J.; Lee, L. T.; Wojtkowski, P. J. Am. Chem. Soc. 1967. 89. 6804.

^{(3) (}a) Brown, H. C.; Kramer, G. W.; Levy, A. B.; Midland, M. M. Organic Synthesis via Boranes; John Wiley & Sons: New York, 1975. (b) Organic Synthesis via Boranes; John Wiley & Sons: New York, 1975. (b)
Brown, H. C.; Ramachandra, P. V. Pure Appl. Chem. 1994, 66, 201–212.
(c) Brown, H. C.; Hydroboration; Benjamin: New York, 1962. (d) Onak,
T. Organoboron Chemistry; Academic Press: New York, 1975.
(4) (a) Matteson, D. S. Acc. Chem. Res. 1988, 21, 294–300. (b) Matteson,
D. S. Tetrahedron 1989, 45, 1859–1885. (c) Pelter, A. In Rearrangements in Ground and Excited States; de Mayo, P., Ed.; Academic Press: New York, 1975.

York, 1980; Vol. 2.

⁽⁵⁾ Corey, E. J.; Chaykovsky, M. J. Am. Chem Soc. 1965, 87, 1353.

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 longchain 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, polymodel 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 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)ethyl)borane, 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, H_2O_2 , NaOH), a quantitative yield of α -(pmethoxyphenyl)- 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 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

$$\underbrace{\begin{array}{c}1) \quad BH_{3} \bullet THF}_{OMe} \\ \underbrace{\begin{array}{c}2) \quad 3n \left[\overrightarrow{CH_{2}-S(O)Me_{2}} \right]}_{2} \\ \underbrace{\begin{array}{c}2) \quad 3m \left[\overrightarrow{CD_{2}-S(O)Me_{2}} \right]}_{3} \\ \underbrace{\begin{array}{c}3) \quad \overline{OOH \ / \ NaOH}}_{m} \\ \end{array}}_{MeO - \underbrace{\left\{ -CH_{2} \left[CH_{2} \right]_{n} \left[CD_{2} \right]_{m} CH_{2}OH \right]}_{m} \\ \end{array}}$$
(4)

tris-((p-methoxyphenyl)ethyl)borane (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/econsistent with a copolymer of α -hydroxy- ω -(p-methoxyphenyl)polymethylene containing $(CH_2)_n(CD_2)_m$ units¹² where 3nand 3m 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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(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. Macro- G. J. Macromolecules 1991, 27, 234. (b) Chung, T. C.; Janvikul, W.; Bernard, R.; Jiang, G. J. Macromolecules 1994, 27, 26. (c) Chung, T. C.; Rhubright, 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.; Henrioulle-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), (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.

⁽⁶⁾ Progress was monitored by removing aliquots, quenching with H_2O 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.

⁽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.