Controlled polymerization of primary acrylates such as *n*-butyl acrylate (*n*BuA) or 2-ethylhexyl acrylate (EHA) is achieved at $-78\,^{\circ}C$. Conversion of the monomer is quantitative, and the resulting polymers have molecular weights as high as 120000 g mol^{-} and narrow molecular-weight distributions ($M_w/M_n < 1.2$; Figure 5).

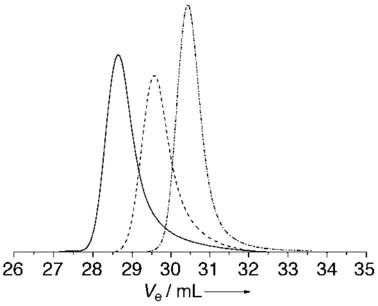

Figure 5. GPC elution diagram for PtBuA (– – – –; $M_n = 70800$, $M_w/M_n = 1.15$), PnBuA (–·–·–; $M_n = 30500$, $M_w/M_n = 1.11$), and PEHA (—; $M_n = 119000$, $M_w/M_n = 1.20$), prepared in a polymerization initiated at $-78\,^{\circ}C$ with EiBLi and $NMe_4^+[Al_2Me_6Cl]^-$.

In summary, we have discovered a new initiating system that takes advantage of readily accessible and inexpensive reagents to produce polymethacrylates and polyacrylates of high molecular weight.

Experimental Section

Reagents: Ethyl α-lithioisobutyrate was prepared from ethyl isobutyrate and lithium diisopropylamide in hexane by described methods.[22] Alkylaluminum compounds were purchased from Aldrich as solutions (25 wt %) in toluene and used without further purification. Tetraalkylammonium halides (Aldrich) were suspended in benzene and freeze-dried. (Meth)-acrylic monomers obtained from BASF AG were fractionally distilled from CaH_2 at reduced pressure through a column (1 m) with Sulzer packing, stirred over CaH_2, degassed, and distilled under high vacuum. Methacryloyl-terminated PMMA macromonomers donated by Röhm GmbH were used as received. Toluene (BASF AG) was fractionally distilled through a 1.5-m column, stirred twice over Na/K alloy, degassed, and distilled under high vacuum.

Polymerizations: All polymerizations were carried out in a stirred tank reactor under a nitrogen atmosphere. The initiator ethyl α-lithioisobutyrate was added to a solution of tetraalkylammonium halide and alkylaluminum compound in toluene, and the mixture was stirred for 5 min, after which the monomer was introduced. Polymerization was quenched with methanol/acetic acid (9/1) and the monomer conversion was determined by GC with octane or decane as internal standard. After evaporation of the solvent, the polymer was dissolved in benzene, the solution was filtered, and the polymer was freeze-dried.

Polymer characterization: Gel permeation chromatography (GPC) was used for molecular-weight distribution analysis, with THF as eluent (flow rate: 1 mL min^{-1}; columns: 60 cm, 5 µm PSS-SDV gel, 100 Å and linear 10^2–10^5 Å; detectors: JASCO-UVIDEC100III and Bischoff RI8110). Appropriate methacrylate and acrylate polymer standards were used to calibrate the columns. The molecular weights of comb-shaped polymers were determined with GPC (on-line viscosity detection) by universal calibration. ^1H and ^{13}C NMR spectra (Bruker AM-400) of the polymers were recorded at room temperature in $CDCl_3$. The α-CH_3 and C=O signals were used for the determination of triad tacticities.

Received: November 27, 1997 [Z11202IE]
German version: *Angew. Chem.* **1998**, *110*, 1461–1463

Keywords: aluminum · polyacrylates · polymerizations · reaction mechanisms

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Polyhomologation: Synthesis of Novel Polymethylene Architectures by a Living Polymerization of Dimethylsulfoxonium Methylide[**]

Kenneth J. Shea,* Brett B. Busch, and Manuel M. Paz

We recently reported a new polymerization reaction for the synthesis of polymethylene, the simplest carbon-backbone polymer constructed one methylene group at a time.[1, 2] The ylide dimethylsulfoxonium methylide (**1**)[3] is the monomer in this reaction and serves as the source of methylene. Polymerization is initiated by trialkylboranes. All three alkyl groups

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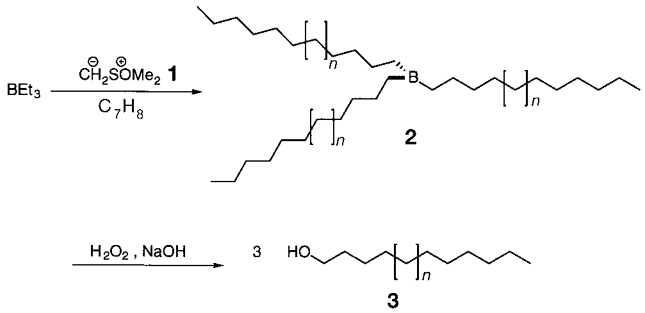
[**] Financial support of this work was provided by the National Science Foundation, Chemistry Division (grant no. CHE-9617475).

on boron participate in the reaction, which gives rise to the star polymethylene organoborane **2** (Scheme 1). Polyhomologation is a living polymerization reaction in which the length of the polymethylene chain is determined by the initial molar ratio of ylide to organoborane. Polydispersities (PDs) that approach the Poisson distribution ($PD = M_w/M_n \approx 1.02-1.01$) have been obtained. These oligomeric and polymeric organoboranes are amenable to a number of synthetic transformations that can be used to functionalize the ends of the polymethylene chains. For example, peroxide cleavage of the carbon–boron bonds in star molecule **2** results in linear polymethylene **3** with terminal hydroxyl groups in yields over 90% (Scheme 1).[1]



Scheme 1. Polyhomologation and subsequent oxidative cleavage.

The star-tris(polymethylene)borane can participate in a number of chemical transformations that result in novel polymethylene architectures not available through conventional ethylene polymerization. We demonstrate this by the synthesis of tris(polymethylene) methanols and polymethylene-substituted cyclooctanes. Our implementation takes advantage of "stitching" transformations available to organoboranes through which all three of the alkyl groups on boron are joined to a new carbon atom.[4] These transformations, when applied to polyhomologated organoboranes, result in the synthesis of star-polymethylene methanols. We also present evidence that the polyhomologation reaction can be initiated by bridged bicyclic organoboranes. Use of these initiators results in cyclic architectures that contain multiple polymethylene substituents.

Two examples serve to illustrate the first strategy. Polymethylene methanols **4** were synthesized by the polyhomologation–chain stitching–oxidation sequence shown in Equation (1). Triethylborane was introduced into a preheated solution of **1** in toluene under N_2 (ratio of ylide: trialkylborane = 60:1). The ylide was consumed within three minutes. To this heated mixture was added α,α-dichloromethyl methyl ether (DCME),[5] followed by dropwise addition of a solution of $LiOCEt_3$ in hexane.[4] After 2 h at 40 °C the resulting polymethylene derivative was oxidized (aqueous NaOH and 30% H_2O_2, heating at reflux for 1 h). Addition of acetonitrile and methanol to the reaction mixture caused precipitation of **4**.[6] In experiments in which the molar ratio of ylide to organoborane was varied from 25 to 60, 90, and 120, the experimentally determined number-average molecular weights (M_n) of the products were 530, 775, 1682, and 1982, respectively, in close agreement with the calculated molecular weights (Table 1). The PDs ranged from 1.02 to 1.13. Careful examination of material eluted during gel permeation chromatography (GPC)[7] revealed the absence of straight-chain oligomer. The melting temperature (T_m) for the sample listed in entry 4 was approximately 85 °C [Eq. (1)].

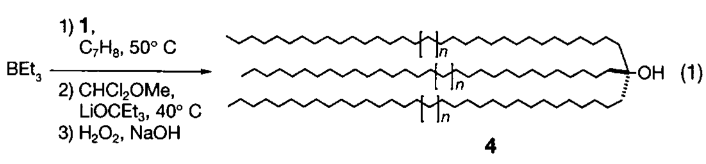
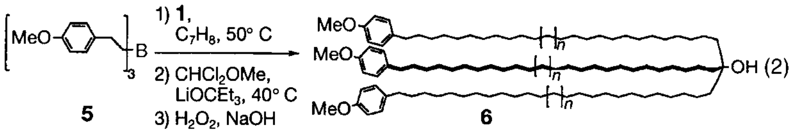


Table 1. GPC analysis of **4**.

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

[a] The calculated molecular weight is based on the theoretical degree of polymerization for the initial ratio of ylide to borane. [b] Determined by GPC analysis.



The preparation of ω-substituted tris(polymethylene) methanols **6** was also accomplished by the polyhomologation–stitching–oxidation sequence. Tris(*p*-methoxyphenyl)borane (**5**), prepared by hydroboration of *p*-methoxystyrene, was used to initiate polyhomologation of ylide **1**. After complete reaction of the ylide and treatment with DCME under basic conditions, polymethylene **6** was obtained in 74% yield [Eq. (2)]. Both NMR spectroscopy[8] and molecular-weight data from GPC[9] were consistent with the assigned structure. In three experiments with molar ratios of ylide to initiator of 45, 90, and 120, the experimentally determined M_n values were 758, 1349, and 1741, respectively (Table 2), again

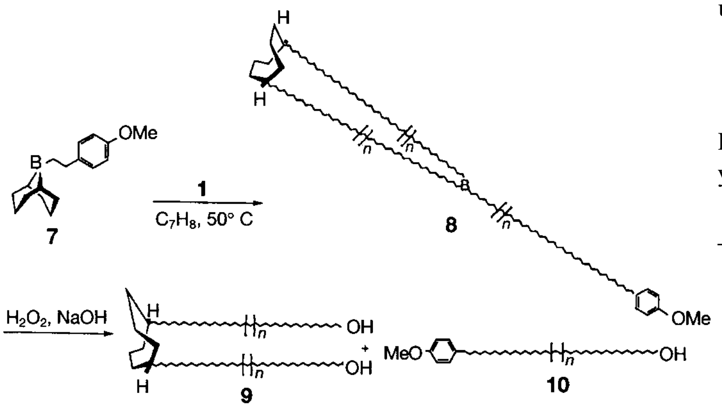
Table 2. GPC analysis of **6**.

Entry	Ylide: Initiator	M (calcd.)[a]	M_n[b]	M_w	PD[b]
1	30	897	714	776	1.08
2	45	1066	758	844	1.11
3	90	1698	1349	1545	1.14
4	120	2119	1741	2155	1.20
5	150	2539	2784	3313	1.19

[a] The calculated molecular weight is based on the theoretical degree of polymerization for the initial ratio of ylide to borane. [b] Determined by GPC analysis.

in close agreement with calculated molecular weights. These polymeric methanols exhibited PD values in the range of 1.08–1.20.

Particularly interesting polymethylene systems can be derived from bridged bicyclic organoboranes. This is illustrated by the synthesis of *cis*-1,5-bis(α-hydroxypolymethylene)cyclooctanes **9**. The starting material, *B*-*p*-methoxyphenylethyl-9-BBN (**7**), is prepared by the hydroboration of *p*-methoxystyrene with 9-BBN (9-BBN = 9-borabicyclo[3.3.1]nonane). The polyhomologation reaction was accomplished by addition of a solution of **7** in THF to ylide **1** in toluene at 50 °C (Scheme 2). After oxidation of the macrocyclic organoborane, the polymethylene product was isolated in 80–90% yield. Based on prior observations of migratory insertions in 9-BBN derivatives, initial methylene insertion reactions are expected to occur at the bridgehead positions.[10] However, once ring expansion has progressed, insertion reactions should take place readily at all three alkyl positions. The polyhomologation reaction is therefore expected to produce greatly expanded borabicyclic structures **8**. Subsequent oxidative cleavage of the carbon–boron bond yields two polymethylene structures. Analysis by GPC[11] and NMR spectroscopy of the resulting product are consistent with a 1:1 mixture of α-*p*-methoxyphenyl-ω-hydroxypolymethylenes **10** and *cis*-1,5-bis(ω-hydroxypolymethylene)cyclooctanes **9**.[12] Interestingly, because narrow distributions of oligomers are generated it is possible to separate the two polymethylene systems by simple chromatography over silica gel. Separation of telechelic **10** from **9** was carried out at 55 °C with a toluene/hexane/EtOAc mixture (8/2/1).[13] Pure **9** was isolated and characterized independently.[14]



Scheme 2. Polyhomologation of **7** and subsequent oxidative cleavage of **8**.

The PDs for polymethylene derivatives **9** were in the range of 1.04–1.15 (Table 3). Initiator **7** does not restrict control over the length of the polymethylene chain. Despite differences in initial insertion rates, molecular-weight results obtained from GPC appear to be a function of the initial ratio of initiator to ylide.

We have described here the preparation of two new polymethylene topologies, polymethylene methanols **4** and **6** and *cis*-1,5-bis(α-hydroxypolymethylene)cyclooctanes **9**. Their syntheses were achieved by polyhomologation of readily available organoborane starting materials. The length of the methylene chain can be controlled by the initial ratio of trialkylborane to ylide. Both **4** and **6**, as well as **9**, can be prepared with PD values less than 1.10. Physical properties of these interesting new polymethylene structures are currently under investigation.

Table 3. GPC analysis of **9**.

Entry	Ylide: Initiator	M_n	M_w	PD
1	30	682[a]	750	1.04
2	35	836[a]	957	1.07
3	102	1298	1497	1.15
4	163	4151	4453	1.07
5	330	10675	11861	1.11

[a] Substance **9** was analyzed after chromatographic separation from **10**.

Received: December 2, 1997 [Z11226IE]
German version: *Angew. Chem.* **1998**, *110*, 1500–1502

Keywords: boron · oligomers · polymerizations · sulfur · ylides

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[5] Dichloromethyl methyl ether is highly toxic! Proper protocols should be observed for its use.

[6] Spectral data for the reaction product are consistent with structure **4**: ^{1}H NMR (500 MHz, CDCl$_3$): $\delta = 1.55$ (m, 6H), 1.25 (s), 0.88 (t, $J = 6.9$ Hz, 9H); ^{13}C NMR (500 MHz, CDCl$_3$): $\delta = 14.1$, 22.7, 29.7, 31.9, 69.0; IR (KBr) $\tilde{\nu} = 3448$, 2920, 2850 cm^{-1}.

[7] GPC was carried out at 100 °C with ultrastyragel columns and a refractive-index (RI) detector. *o*-Xylene was used as the eluent, and polymethylene samples were prepared as 0.5–0.6% solutions. The GPC calibration curve was prepared with polyethylene standards obtained from Polymer Laboratories and Scientific Polymer Products. For the calibration curve, $R^2 = 0.99978$.

[8] ^{1}H NMR (500 MHz, CDCl$_3$): $\delta = 7.08$ (d, $J = 8.4$ Hz, 6H), 6.82 (d, $J = 8.4$ Hz, 6H), 3.78 (s, 9H,), 2.53 (t, $J = 7.7$ Hz, 6H), 1.56 (t, $J = 8.0$ Hz, 6H), 1.25 (s); ^{13}C NMR (500 MHz, CDCl$_3$): $\delta = 135.1$, 129.3, 113.7, 74.5, 55.3, 35.1, 31.8, 29.7, 29.6, 23.5; IR (KBr): $\tilde{\nu} = 3448$, 2920, 2850, 1469, 1246 cm^{-1}.

[9] The RI response to **6** was opposite to that for **10**.

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[11] GPC analysis revealed incompletely resolved product peaks.

[12] Analysis of the end groups by integration of the ^{1}H NMR signals of **9** and **10** showed the presence of a 1:1 mixture.

[13] R_f values for TLC (toluene/hexane/EtOAc 8/2/1): **10**: 0.5, **9**: 0.1.

[14] ^{1}H NMR (500 MHz, C_7D_8): $\delta = 1.35$ (s), 1.53 (m, 4H), 1.65 (m, 4H), 1.80 (m, 2H), 3.36 (t, $J = 6$ Hz, 4H); ^{13}C NMR (500 MHz, C_6D_6): $\delta = 27.9$, 30.1, 30.6, 33.3, 34.2, 38.1, 39.3, 62.8; ^{13}C NMR (500 MHz, CDCl$_3$): $\delta = 25.5$, 29.7, 30.0, 32.9, 33.7, 38.9, 63.1; IR (KBr): $\tilde{\nu} = 3448$, 2920, 2850 cm^{-1}; GPC: $M_n = 972$, $M_w = 1008$, PD = 1.03; elemental analysis calcd for $C_{67}H_{134}O_2$ ($M_n = 972.01$): C 82.78, H 13.92; found: C 82.78, H 13.90.