Living Polymerization of Sulfur Ylides. Synthesis of Terminally Functionalized and Telechelic Polymethylene

Brett B. Busch, Chad L. Staiger, Jonathan M. Stoddard, and Kenneth J. Shea*

Department of Chemistry, University of California, Irvine, Irvine, California 92697-2025

Received May 13, 2002; Revised Manuscript Received August 12, 2002

ABSTRACT: The boron-catalyzed polymerization of dimethylsulfoxonium methylide (**1**) has been used to prepare telechelic polymethylene polymers. The functional polymers were synthesized by hydroboration of substituted α-olefins. Functional groups including biotin, carbohydrates, primary and secondary amines, and dansyl and pyrene fluorescent groups were tolerant to the reaction conditions. The living polymerization of ylide **1** was initiated and catalyzed by the organoborane. Oxidation of the resulting tris(polymethylene) organoborane produced *ω*-hydroxy-terminated polymethylenes. The reactions were used to produce α,*ω*-polymethylenes with molecular weights in the range of 1000−17 000 with polydispersities < 1.1.

Introduction

Polymers that contain functional groups at both termini of the chain have found utility in the synthesis of block copolymers[1] for polymeric networks,[2−4] as blending agents,[5−7] and as surface modifiers.[8,9] Telechelic polymers have traditionally been synthesized using anionic,[10,11] radical,[12−14] ring-opening,[15−18] and olefin metathesis[19−21] polymerizations.

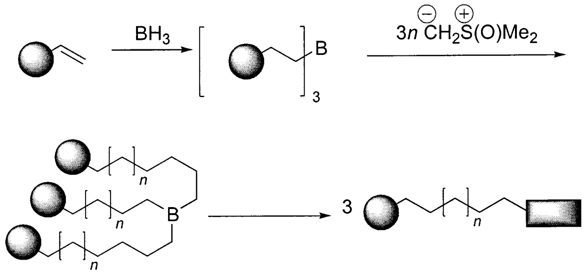
Telechelic polyethylene has been produced by the hydrogenation of telechelic polybutadiene (PBD).[22] The anionic and controlled radical polymerization of butadiene introduces minor amounts of branches.[23−25] More recently, the ring-opening metathesis polymerization of cyclooctadiene has been used to prepare telechelic PBD without branching.[26] A homogeneous metal coordination catalyst developed by Brookhart has been successfully applied to the synthesis of telechelic polyethylene.[27]

We have reported a synthesis of linear polymethylene from the polymerization of dimethylsulfoxonium methylide (**1**) using organoboranes as initiators.[28−33] The living polymerization produces linear polymethylene with typical PDI's < 1.1. The reaction has recently been applied to the synthesis of substituted carbon backbone polymers.[34] The present report describes the development of this reaction for introducing a variety of functional groups at the α-chain end.

For simple trialkylboranes all three alkyl groups on boron undergo homologations, giving rise to a star polymethylene borane (Scheme 1). The polymerization of dimethylsulfoxonium methylide (**1**) produces linear, narrow molecular weight distributions of polymethylene with theoretical degrees of polymerization $DP_t = [\text{ylide}]/3[R_3B]$. The star polymethylene organoboranes are amenable to synthetic transformations that can be used to terminate the polymethylene chain with functionality.[35−38] For example, the boron−carbon bond can be oxidatively cleaved (with trimethylamine-*N*-oxide) to yield hydroxypolymethylene.[33]

The α- and *ω*-positions of the polymethylene chain may be differentially functionalized by a combination of functional trialkylborane initiator/catalyst and subsequent chemical transformations of the resulting star polymethylene borane. Functionality at the α-chain end arises from the original substituents on the alkyl borane. These are available by hydroboration of functional α-olefins. The functional groups are limited by their compatibility with hydroboration and the subsequent polyhomologation. Functionality of the *ω*-chain end is achieved by any one of a myriad of chemical transformations available to trialkylboranes.[35−38]

Scheme 1. Schematic Representation of the Synthesis of Telechelic Polymethylene Derivatives



We have chosen a range of functional groups to implement this methodology. The pyrene and dansyl groups have been used as fluorescent probes to analyze surface properties, solvent accessibility, and mobility of polymers.[39−41] Carbohydrate and biotin-functionalized polymethylene polymers have potential for use in diagnostic arrays of proteins, cells, or DNA.[42−46] The accessibility and activity of molecules bound to solid-phase media have been shown to increase with the use of various spacers.[47,48] In particular, PEG spacers have been used to ensure aggregation and display of functional groups at the surface of polyethylene.[39] Amino-terminated polymethylene has potential applications for its use in block copolymer synthesis, surfactants, metal complexation agents, and stabilizers for polyethylene.[49−53]

Synthesis of Functional Olefins

The polyhomologation reaction utilizes organoborane initiators that can be prepared from olefins via hydroboration. This methodology makes available complex functional organoboranes (Figure 1). To illustrate, we have chosen olefins containing the fluorescent groups dansyl and pyrene both with and without a short poly(ethylene glycol) spacer. In addition, we have also employed protected biotin, glucose, and mannose functionalities.

10.1021/ma020729n CCC: $22.00

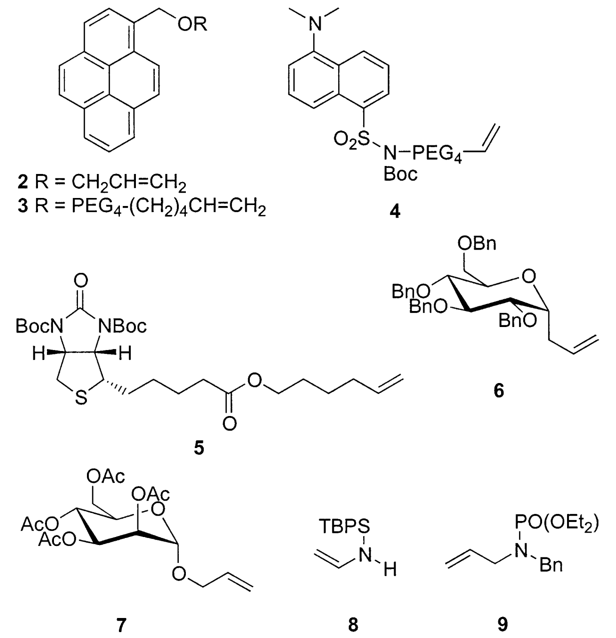
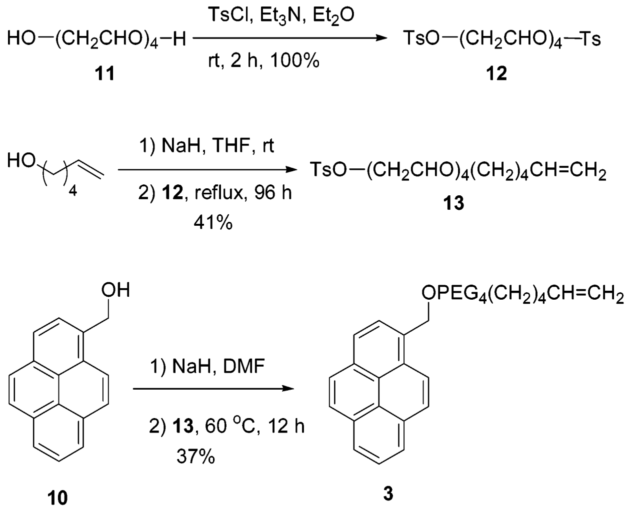


Figure 1. Functional olefins **2**–**9** used for the hydroboration–polyhomologation–oxidation sequence to produce telechelic polymethylenes.

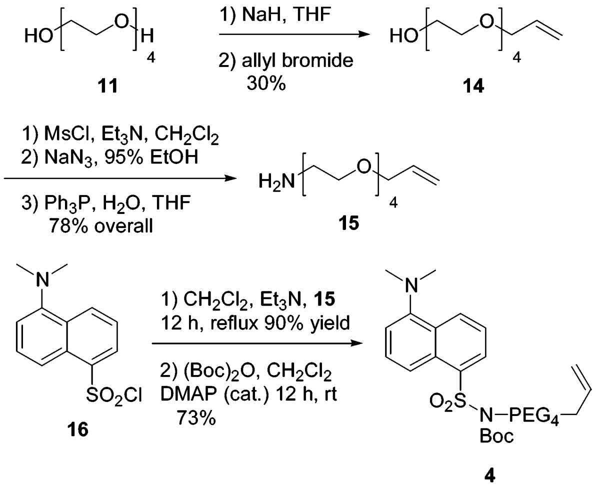
Scheme 2. Synthesis of *O*-1-Methylpyrene, *O*-5-Hexenyl Tetraethylene Glycol (3)



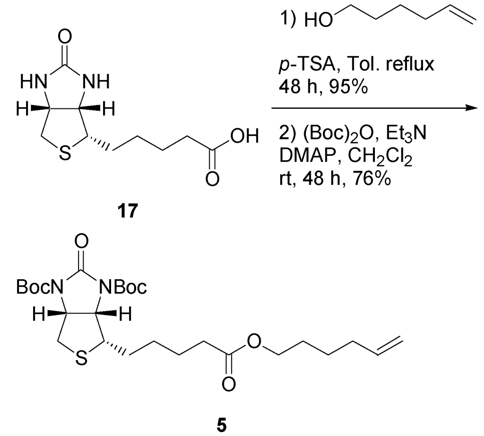
The pyrene-functionalized olefins were synthesized according to Scheme 2. Synthesis of 1-allyl-oxymethyl pyrene (**2**) was accomplished by alkylating 1-hydroxymethylpyrene (**10**) with allyl bromide in 95% yield. For the synthesis of the pegylated derivative **3**, tetraethylene glycol (**11**) was converted to the tetraethylene glycol ditosylate (**12**) by reaction with TsCl and Et_3N in ether at room temperature (Scheme 2). Displacement of the tosylate with 5-hexene-1-ol resulted in a statistical distribution of products. The monosubstituted product **13** was produced in 41% yield based on recovered starting material. Reaction of **13** with 1-hydroxymethylpyrene (**10**) with NaH in DMF produced olefin **3** in 37% yield.

The synthesis of 5-(dimethylamino)-1-sulfonate (dansyl) olefin **4** required protection of the sulfonamide group (pK_a = 13) to prevent coordination[54] and protolysis of BH_3. The synthesis is outlined in Scheme 3. Tetraethylene glycol (**11**) was alkylated with allyl bromide in THF to afford *O*-allyl tetraethylene glycol ether (**14**) in 30% isolated yield. The terminal hydroxy was converted to the amine **15** by literature methods.[55,56] The coupling of dansyl chloride **16** with amine **15** was accomplished in refluxing CH_2Cl_2/Et_3N in 90% yield. Subsequent protection with $(Boc)_2O$ in the presence of catalytic DMAP afforded Boc-protected, dansyl olefin **4** in 73% yield.

Scheme 3. Synthesis of Boc-Protected, Dansyl Olefin 4 Using Amino-PEG Spacer 15



Scheme 4. Synthesis of Bis-Boc-Protected, Biotin Olefin 5



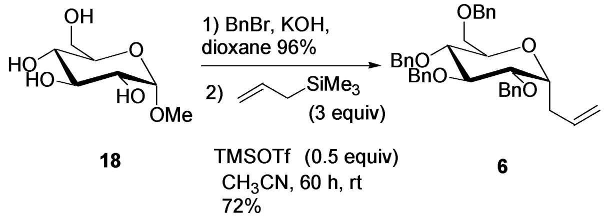
The synthesis of the biotin olefin **5** required protection of the imidazole group due to its ease of reduction in the presence of BH_3.[57] The synthesis is outlined in Scheme 4. The Fischer esterification of (+)-biotin (**17**) with 5-hexene-1-ol proceeded in refluxing toluene over 48 h to give the ester in 95% yield. Subsequent protection with $(Boc)_2O$ afforded protected, biotin olefin **5** in 76% yield.

The synthesis of tetrabenzyl-*C*-allylglucopyran (**6**) was prepared (Scheme 5) from α-methoxy-D-glucose (**18**) by published procedures.[58] A 9:1 mixture of α and *β* isomers was obtained.

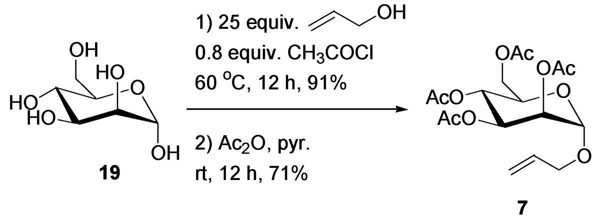
O-Tetraacetate *O*-allyl mannoside (**7**), as a 9:1 mixture of α and *β* isomers, was synthesized from α-D-mannose (**19**) (Scheme 6) according to published procedures.[59]

Hydroboration of primary amino olefins normally requires a large excess of hydroborating reagent due to the coordinative ability of primary amines toward borane.[60] The polyhomologation methodology requires hydroboration with 3.5 equiv of olefin to ensure only one

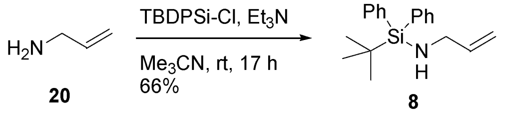
Scheme 5. Synthesis of Tetrabenzyl-*C*-allyl Glycoside (6)



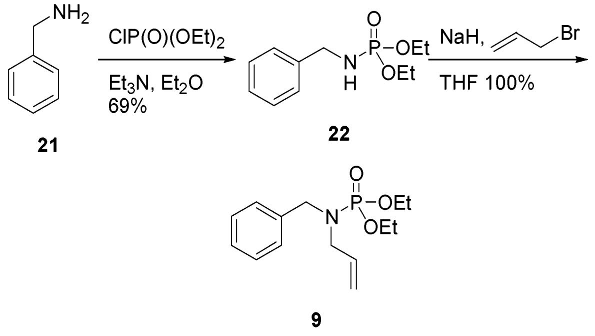
Scheme 6. Synthesis of Tetraacetate Mannose Olefin 7



Scheme 7. Synthesis of Silyl-Protected, Allyl Amine 8



Scheme 8. Synthesis of Phosphoroamidate-Protected Benzyl Amine 9



type of initiator, a trialkylborane, is present during polymerization. An excess of borane would produce a mixture of borane initiators (RBH_2, R_2BH, R_3B), each capable of undergoing polyhomologation. To address these issues, we chose protection of allylamine (**20**) with *tert*-butyldiphenylsilyl chloride (TBDPSi−Cl) to suppress amine coordination to boron. Silylation increases the steric bulk at nitrogen.[60] The synthesis of silyl-protected allylamine **8** is shown in Scheme 7. Allylamine **20** was reacted with TBDPSi−Cl in the presence of triethylamine to give protected olefin **8**.[61]

The synthesis of a protected secondary amino olefin **9** is shown in Scheme 8.[62] Reaction of benzylamine **21** with diethyl chlorophosphate afforded phosphoroamidate **22**, which was quantitatively alkylated with NaH and allyl bromide to produce the protected amino olefin **9**.

Scheme 9. Synthesis of ω-Hydroxypolymethylene 25 from an α-Olefin

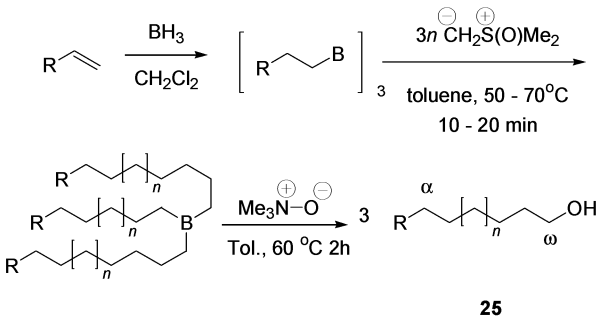
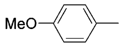
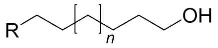


Table 1. Molecular Weight Data for Telechelic Polymethylene 25a−d[a]

Entry	Functional Group	M_n	M_w	PDI
1		640	650	1.02
2		690	700	1.01
3		1 670	1 750	1.05
4	**25a**	2 250	2 320	1.03
5		5 420	5 640	1.04
6		15 000	16 700	1.19
7	MeS—	770	790	1.02
8	**25b**	3 230	3 320	1.03
9		680	710	1.04
10	Me_3Si— **25c**	1 270	1 430	1.12
11		3 220	3 780	1.17
12	$^nBu_3Sn$—	565	570	1.01
13	**25d**	8 410	8 610	1.02

[a] All samples are ω-hydroxy-terminated.



25a: R = 4-MeO-C_6H_4, **25b**: R = MeS,
25c: R = Me_3Si, **25d**: R = Bu_3Sn

Figure 2. ω-Hydroxy polymethylene targets from commercially available olefins.

Hydroboration and Polyhomologation of "Simple" Functional Olefins

The introduction of functionality at the termini of polymethylene chains is illustrated by the reaction sequence shown in Scheme 9. Functional trialkylboranes were prepared by hydroboration of commercially available olefins: 4-vinylanisole, allyltrimethylsilane, allyl methyl sulfide, and vinyl tri-*n*-butyltin with borane·THF or borane·Me_2S in CH_2Cl_2.[63,64] In a typical polyhomologation reaction, an aliquot of trialkylborane initiator was rapidly added to a preheated solution of dimethylsulfoxonium methylide (**1**) in toluene at 50−70 °C. Initiation of polyhomologation is instantaneous, and the consumption of the ylide was monitored by titration. Following consumption of ylide **1** (ca. 5−10 min), the chain-cleavage reaction was achieved by oxidation with trimethylamine-*N*-oxide (TAO) or basic hydrogen peroxide to prepare ω-hydroxypolymethylene (Figure 2). Oxidation with TAO is preferred since fewer side reactions occur.[33] Telechelic polymethylenes were precipitated with acetonitrile and isolated via vacuum filtration (60−95% yield).

Quantitative incorporation of the functional end group was confirmed by ^1H NMR. For example, the ^1H NMR spectrum of ω-hydroxy-α-(*p*-methoxylphenyl)polymethylene **(25a)** revealed the methoxy protons (δ 3.79, 3H), hydroxy-bearing terminal methylene (δ 3.64, 2H), and benzyl methylene (δ 2.54, 2H) in the ratio of 1.5:1:1. Molecular weight data for the telechelic polymethylenes **25a−d** were obtained from GPC analysis (Table 1). In most examples, the average molecular weights (M_n) were accurately controlled from the ratio of ylide **1** to trialkylborane. The data in entry 6 describe an experiment where tris-(p-methoxyphenylethyl)borane was added to 3000 mol equiv of ylide **1** ($DP_t = 1000$, $MW_t = 14\,100$), in close agreement with the number-average molecular weight ($M_n = 14\,970$) that was determined from GPC. The polydispersity index (PDI) of higher molecular weight polymers increased slightly in some cases but remained low (Table 1). The functional trialkylboranes generated telechelic polymethylene with PDI's below 1.1 at degrees of polymerization ranging from 20 to 600, except in a few cases. The PDI of ω-hydroxy-α-trimethylsilylpolymethylene **(25c)**, however, is somewhat higher than average (Table 1, entries 9−11).

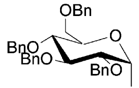
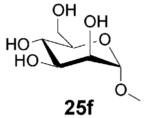
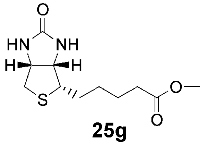
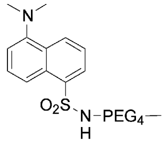
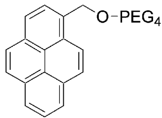
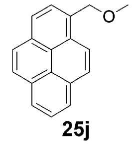
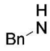
Polyhomologation of Functional α-Olefins

α-Olefins **2**−**9** (Figure 1) were hydroborated with $BH_3{\cdot}SMe_2$ or $BH_3{\cdot}THF$ in CH_2Cl_2 according to Scheme 1. An aliquot of the freshly prepared organoborane solution was added to 3n equivalents of ylide **1**. Following consumption of ylide (ca. 10 min), the resulting homogeneous solution was oxidized with trimethylamine-N-oxide in toluene at 60 °C, and then the polymers were precipitated with acetonitrile. Polymers with protecting groups (from olefins **4**, **5**, **7**, **8**, and **9**) were redissolved in toluene. The Boc, acetyl, silyl, and phosphoroamidate protecting groups were removed by stirring with trifluoroacetic acid (10 equiv, 80 °C, 1 h), sodium hydroxide (80 °C, 2 h), 10% HCl (80 °C, 15 h), and 10% HCl (80 °C, 1 h), respectively. The benzyl protecting groups were not removed from the carbohydrate terminus of polymethylene **25a**. Reprecipitation with acetonitrile afforded the deprotected, functionalized ω-hydroxy polymethylene polymers **25e**−**l**. The molecular weight analyses for **25e**−**k** are shown in Table 2.

The functional α-olefins **2**−**9** are compatible with hydroboration, polyhomologation, and oxidation to produce telechelic polymethylene polymers **25a**−**l** from 66% to 83% yield. The differences between the targeted and experimental degrees of polymerization were no more than 10−20% with the exception of **25g** and **25l**. All the polymers displayed monomodal GPC distributions. The PDI was lower than 1.1 in most cases and increased slightly at higher molecular weights (Table 2, entry 9). The primary, amine-terminated polymethylene **25l** could not be analyzed by GPC (RI detector), presumably due to the coincidence of the diffractive index between the polymer and o-xylene. The degree of polymerization was obtained by end-group analysis using ^{1}H NMR (Table 3).

There was a large difference between the theoretical (DP_t) and experimental (DP_e) degrees of polymerization for **25l** (Table 3, entries 1 and 2). Similarly, the DP_t and DP_e for biotin-terminated polymethylene **25g** were 18 and 252 (Table 2, entry 6). We attribute these differences to incomplete hydroboration due to the interference of Lewis basic sites available for coordination to borane. Kinetic studies of hydroboration have demonstrated that borates are ineffective at hydroboration, and BH_3 must decomplex from any coordinating molecules to hydroborate olefins.[65] We suspected that the hydroboration step did not go to completion. When the hydroboration of **8** was carried out at 45 °C for >4 h, the organoborane initiator afforded amino-terminated polymethylene **25l** with a smaller difference between the theoretical and experimental degrees of polymerization.

Table 2. Average Molecular Weight Data for Telechelic Polymethylene 25a−k[a]

Entry	Functional Group	M_n	M_w	PDI
1	 **25e**	920	940	1.02
2		1 720	1 750	1.02
3		4 020	4 080	1.01
4	 **25f**	7 060	7 450	1.06
5		19 900	21 700	1.09
6	 **25g**	3 860	3 960	1.02
7		4 310	4 410	1.02
8	 **25h**	8 330	8 580	1.03
9		17 200	18 600	1.08
10	 **25i**	10 500	11 100	1.06
11		14 600	15 600	1.07
13	 **25j**	1 470	1 510	1.03
14		3 290	3 360	1.02
15		8 710	9 140	1.05
16	 **25k**	630	660	1.05[b]
17		940	1 010	1.07[b]

[a] M_n and M_w were obtained from GPC. All polymers are ω-hydroxy-terminated. [b] ESI-MS.

Table 3. End-Group Analysis for ω-Hydroxy-α-aminopolymethylene 25l Using Organoborane Initiator Produced under Different Reaction Conditions[a]

entry	functional group	hydroboration conditions	DP_t	DP_e
1	H_2N-	22 °C, 24 h	25	95
2		22 °C, 24 h	50	195
3		45 °C, 4h	75	108

[a] DP_e determined from ^{1}H NMR end-group integration.

MALDI−TOF and ESI-MS Analysis

The crystallinity and the absence of polar functionality limits the utility of MALDI−TOF for the characterization of polyethylene.[66] Recent efforts to optimize the ionization of polyethylene include using lasers of variable intensity and wavelength,[67] first-row transition-metal ions,[68] and various matrixes (pyrene, perylene, 9-nitroanthracene, *all-trans*-retinoic acid, dithranol, 2,5-dihydroxybenzoic acid, and *trans,trans*-1,4-diphenyl-1,3-butadiene)[69] have shown promise. In all cases mass spectrometry has been restricted to the analysis of lower molecular weight polyethylene, MW < 2000 amu. The incorporation of polar functionality at the termini of polymethylene was expected to enhance the prospects for analysis by mass spectrometry.

Simple α-hydroxypolymethylene (MW < 2000) and α-amino-ω-hydroxypolymethylene **(25l)** (MW = 1330) do

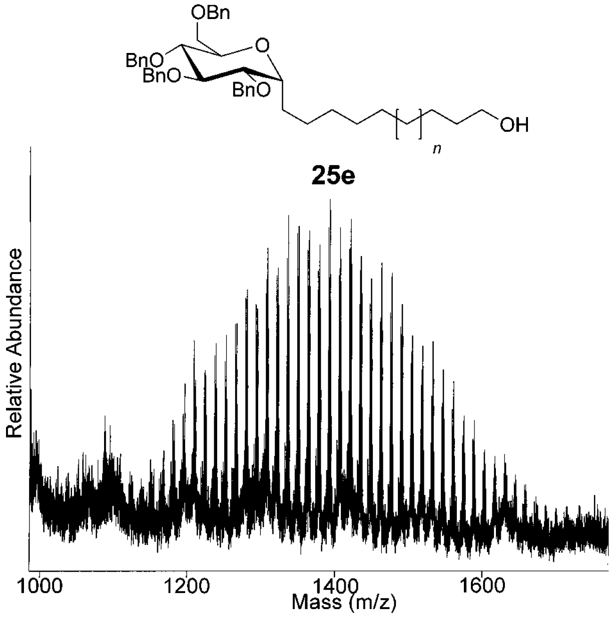


Figure 3. MALDI−TOF mass spectrum of ω-hydroxy-α-(tetra-*O*-benzylglucopyran)-*C*-polymethylene (**25e**) $(M + Ag)^+$ showing a monodisperse distribution with $M_n = 1176$, $M_w = 1200$, and PDI = 1.02.

not ionize under a variety of MALDI conditions. Upon examination of selected functional polymethylene samples, it was found that methyl sulfide, sodium sulfonate, *p*-anisole, pyrene, and tetra-*O*-benzylglucopyran functionality located at the terminus of hydroxy polymethylene facilitates the ionization and desorption of molecular ions by MALDI, permitting MS analysis of low molecular weight polymethylene (MW < 2000).[70]

In the present study, 2 μL each of a heated solution of polymer (0.2 mM in toluene) and matrix (dithranol/AgOTf 0.2 M in toluene) were codeposited onto a stainless steel sample stage. During mixing and cooling, precipitation of the polymer was evident. The samples were air-dried at room temperature for 15 min before analysis.

For example, Figure 3 shows a MALDI−TOF mass spectrum of α-hydroxy-ω-(tetra-*O*-benzylglucopyran)-*C*-polymethylene (**25e**). Each main peak $(M + Ag)^+$ in the mass spectrum is separated by 14.03 mass units, a signature of polymethylene. The calculated molecular weight by MALDI, $M_n = 1176$ (DP = 35), is in closer agreement to the theoretical molecular weight ($DP_t = 40$) than obtained by GPC, $M_n = 924$ (DP = 24). The large polar carbohydrate end group, and particularly the benzyl protecting groups, assist in the ionization of this polymer.

The MALDI−TOF mass spectrum of α-methyl sulfide-ω-hydroxy polymethylene (**25b**) is shown in Figure 4. The ability of sulfur, despite its small size relative to the polymer, to coordinate to silver contributes to the excellent signal-to-noise of the spectrum of this oligomeric polymethylene (DP = 45). When higher molecular weights (MW = 2500) were analyzed for **25e** and **25b**, the signal-to-noise ratio decreased.

Ionization and desorption of α-benzylamino-ω-hydroxyl polymethylene (**25k**) was not successful by MALDI−TOF using the conditions described above. This polymer, however, was readily analyzed by electrospray ionization mass spectroscopy (Figure 5). The benzylamine end group assists in ionization of this low molecular weight sample to produce a distribution of $(M + Na)^+$ ions.

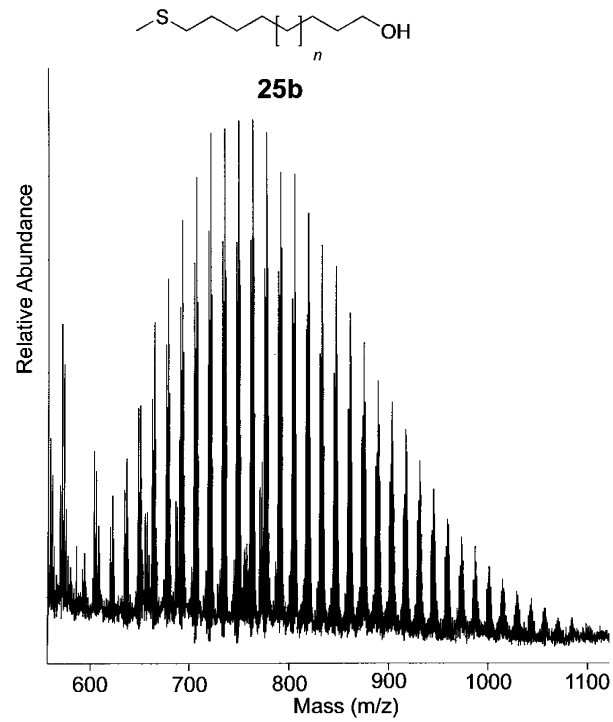


Figure 4. MADLI-TOF mass spectrum of ω-hydroxy-α-methyl sulfide polymethylene (**25b**) $(M + Ag)^+$. $M_n = 695$, $M_w = 721$, PDI = 1.04.

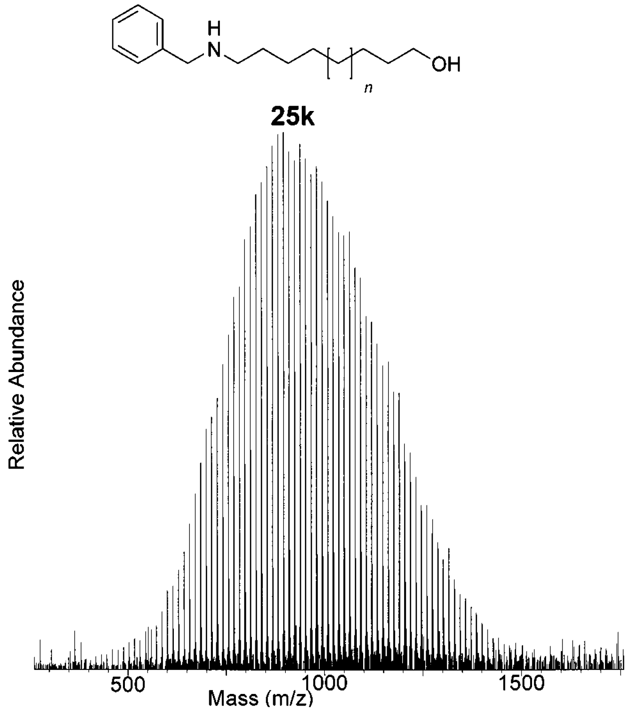


Figure 5. ESI-MS mass spectrum of ω-hydroxy-α-benzylamine-polymethylene **25K** $(M + Na)^+$. $M_n = 942$, $M_w = 1006$, PDI = 1.07.

Conclusion

A general method for the synthesis of telechelic polymethylene has been developed. Functional trialkyboranes are used as the initiator/catalyst resulting in polymethylene terminated with hydroxy, aryl, organosilane, organotin, methyl sulfide, vinyl, carbohydrate groups, biotin, and fluorescent moieties. Quantitative incorporation of the functional group at the termini of the telechelic polymethylene was demonstrated by ^{1}H NMR end group analysis. The polyhomologation reaction allows for control over the molecular weight and produces oligomers and polymers with low polydispersities.

Experimental Section

Instrumentation. ^{1}H and ^{13}C NMR spectra were obtained using either Omega-500 or DRX-500 instruments at 500 and 125 MHz, respectively, and calibrated with residual undeuterated toluene-d_8 and $CDCl_3$. GPC data were obtained using a Waters 150-C instrument using *o*-xylene as the eluent at 100 °C at 1 mL/min. The calibration curve ($R^2 = 0.999\,78$) was made using polyethylene standards from Polymer Labs. The MALDI−TOF spectra were obtained on a PerSeptive Biosystems Voyager-DE Biospectrometry workstation equipped with a nitrogen laser (emission at 337 nm, 3 ns bursts) and a linear detector. Dithranol (1,8,9-anthracenetriol) and silver trifluoroacetate were used as the matrix for MALDI−TOF analyses. Elemental analyses were done at Atlanta Microlab, Inc. Melting point analyses were performed on a Thomas-Hoover uni-melt melting point apparatus and are uncorrected.

Materials. Solutions of ylide **1** in toluene were synthesized as previously described.[33] THF, Et_2O, and CH_2Cl_2 were passed through activated alumina columns under Ar, MeOH was distilled from $Mg(OMe)_2$, Et_3N was distilled from CaH_2, anhydrous DMF was purchased from EM Science, and methanesulfonyl chloride was distilled in vacuo prior to use. Dansyl chloride (Acros) was heated with $POCl_3$ and PCl_3 for 12 h prior to use. All other chemicals were used as received without further purification. All reactions were performed in flame-dried glassware under an atmosphere of N_2.

Sample Procedure for Hydroboration. Tris(4-Methoxyphenylethyl)borane. A solution of $BH_3{\cdot}THF$ (1.0 M in THF, 0.56 mL, 0.56 mmol) was added over 5 min to solution of 4-vinylanisole (0.25 mL, 1.9 mmol) in THF (2.4 mL) at 0 °C. (Alternatively, 1.0 M $BH_3{\cdot}Me_2S$ in CH_2Cl_2 may be used.) 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.^{1}H NMR (500 MHz, $CDCl_3$): δ 7.1 (2H, d, J = 8.4 Hz), 6.85 (2H, d, J = 8.4 Hz), 3.8 (3H, s), 2.65 (2H, t, J = 7.5 Hz), 1.25 (2H, t, J = 7.6 Hz). ^{13}C NMR (125 MHz, $CDCl_3$): δ 130, 128.9, 113.7, 55.2, 37.3, 25.6. ^{11}B NMR (160 MHz, CH_2Cl_2): δ 80.2. HRMS (FAB/CI): *m/z* calcd for $C_{27}H_{34}O_3B$ $(M + H)^+$ 411.2131; found 411.2139.

Sample Procedure for Polyhomologation and Oxidation. ***ω*-Hydroxy-α-(4-methoxyphenyl)polymethylene (25a).** Tris(4-methoxyphenylethyl)borane (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, and THF (5 mL), NaOH (6 M, 0.2 mL, 1.2 mmol), and H_2O_2 (30%, 0.2 mL, 1.2 mmol) were added at 0 °C and stirred at room temperature 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, 100 H); $DP_{exp} = 50$. ^{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): ν_{max} 3448, 2919, 2850 cm^{-1}. FDMS analysis: $M_p = 770$, PDI = 1.02. GPC analysis: $M_n = 690$, $M_w = 700$, 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.

***ω*-Hydroxy-α-methyl Sulfide Polymethylene (25b).** 172 mg (91%) of white solid. ^{1}H NMR (500 MHz, C_6D_6): δ 3.41 (t, 2H, J = 6.2 Hz), 2.35 (t, 2H, J = 7.2 Hz), 1.88 (s, 3H), 1.55 (m, 2H), 1.38 (s, 127 H); DP = 54. ^{13}C NMR (125 MHz, C_6D_6): δ 62.8, 34.7, 33.3, 30.1, 30.0, 29.9, 29.8, 29.1, 26.2, 15.4. IR (KBr): ν_{max} 3348, 2922, 2850, 1437 cm^{-1}. MALDI−TOF: M_n = 695, $M_w = 721$, PDI = 1.04. GPC analysis: $M_n = 600$, M_w = 620, $M_p = 630$, PDI = 1.03. Anal. Calcd for $C_{30}H_{62}OS$: C, 76.52; H, 13.28. Found: C, 76.69; H, 12.89.

***ω*-Hydroxy-α-trimethylsilylpolymethylene (25c).** 132 mg (88%) of white solid. ^{1}H NMR (500 MHz, $CDCl_3$): δ 3.64 (q, 2H, J = 6.0 Hz), 1.57 (m, 2H), 1.25 (s, 68H), 0.47 (br s, 2H), −0.04 (s, 9H). ^{13}C NMR (125 MHz, $CDCl_3$): δ 63.1, 33.6, 29.7, 29.6, 29.4, 25.7, 23.9, 16.7, −1.65. IR (KBr): ν_{max} 3420, 2935, 2860, 1493, 1268 cm^{-1}. GPC analysis: $M_n = 990$, M_w = 1000, $M_p = 1000$, PDI = 1.01. Anal. Calcd for $C_{78}H_{160}OSi$: C, 82.02; H, 14.13. Found: C, 82.05; H, 14.24.

***ω*-Hydroxy-α-(tri-*n*-butyltin)polymethylene (25d).** 220 mg (58%) of white solid. ^{1}H NMR (500 MHz, $CDCl_3$): δ 3.64 (t, 2H, J = 6.6 Hz), 1.67 (m, 8H), 1.51 (m, 10H), 1.36 (m, 8H), 1.26 (s, 80H), 0.89 (t, 9H, J = 7.1 Hz), 0.79 (t, 8H, J = 8.0 Hz). ^{13}C NMR (125 MHz, $CDCl_3$): δ 63.1, 34.2, 32.8, 29.7, 29.3, 29.2, 27.4, 27.0, 25.7, 13.7, 8.8. IR (KBr): ν_{max} 3320, 2960, 2924, 2850, 1470 cm^{-1}. Anal. Calcd for $C_{47}H_{98}OSn$: C, 70.62; H, 12.37. Found: C, 70.51; H, 12.20.

***ω*-Hydroxy-α-(tetra-*O*-benzylglucopyran)-*C*-polymethylene (25e).** 225 mg (73%) of white solid. ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.32 (m, 16H), 7.13 (m, 4H), 4.93 (d, 2H, J = 11 Hz), 4.84 (t, 2H, J = 7.0 Hz), 4.70, (m, 2H), 4.65 (m, 2H), 4.50 (t, 2H, J = 11 Hz), 4.06 (m, 1H), 3.84−3.68 (m, 4H), 3.64 (t, 2H, J = 6.7 Hz), 1.56 (m, 2H), 1.25 (s, 44H). ^{13}C NMR (125 MHz, $CDCl_3$): δ 138.8, 138.3, 138.2, 138.1, 128.4, 128.3, 127.8, 127.6, 122.3, 82.6, 80.4, 78.3, 75.4, 75.0, 74.0, 73.4, 72.9, 70.9, 69.1, 63.0, 32.8, 29.7 (m), 29.4, 25.7, 25.3, 24.5. IR (KBr): ν_{max} 3446, 3040, 3032, 2929, 2850, 1456, 1090 cm^{-1}. MALDI−TOF MS M_n = 1110, PDI = 1.01. GPC analysis: $M_n = 730$, M_w = 740, PDI = 1.02. Anal. Calcd for $C_{82}H_{131}O_6$: C, 80.13; H, 10.75. Found: C, 80.29; H, 10.91.

***ω*-Hydroxy-α-mannose Polymethylene (25f).** 147 mg (85%) of white solid. ^{1}H NMR (500 MHz, toluene-d_8, 80 °C): δ 4.64 (m, 1H), 3.69 (m, 2H), 3.62 (m, 1H), 3.52 (m, 2H), 3.38 (m, 2H), 2.53 (m, 1H), 1.84 (m, 1H), 1.73 (m, 1H), 1.65 (m, 1H), 1.34 (br s, 840H). IR (KBr): ν_{max} 3420 (br), 2918, 2850, 1466, 815 cm^{-1}. GPC analysis: $M_n = 7060$, $M_w = 7450$, PDI = 1.06.

***ω*-Hydroxy-α-biotin Polymethylene (25g).** 65 mg (35%) of white solid. ^{1}H NMR (500 MHz, toluene-d_8, 50 °C): δ 4.04 (t, J = 6.6 Hz, 4H), 3.61 (m, 2H), 3.54 (m, 2H), 3.37 (t, J = 6.4 Hz, 2H), 2.62 (m, 2H), 2.32 (dd, J = 7.3, 5.1 Hz, 2H), 1.34 (m, 236H), 0.88 (m, 6H). $DP_{NMR} = 236$. IR (KBr): ν_{max} 3422, 2919, 2850, 1474, 719 cm^{-1}. GPC analysis: $M_n = 3860$, $M_w = 3960$, $M_p = 3840$, PDI = 1.02.

***ω*-Hydroxy-α-(dansyl tetraethylene glycol) Polymethylene (25h)**. 82 mg (46%) of white solid. ^{1}H NMR (500 MHz, toluene-d_8, 80 °C): δ 1.38 (br s). IR (KBr): ν_{max} 3396, 2919, 2850, 1464, 1144, 719 cm^{-1}. GPC analysis: $M_n = 8330$, M_w = 8580, $M_p = 8860$, PDI = 1.03.

***ω*-Hydroxy-α-(1-pyrene-methyl tetraethylene glycol ether) Polymethylene (25i)**. 0.33 g (83%) of white solid. ^{1}H NMR (500 MHz, toluene-d_8, 80 °C): δ 8.31 (d, J = 9.2 Hz, 1H), 7.92 (m, 5H), 8.00 (d, J = 13.7 Hz, 1H), 7.38 (d, J = 13.5 Hz, 1H), 7.74 (t, J = 7.62 Hz, 1H), 5.11 (s, 2H), 3.64 (td, J = 4.9, 1.7 Hz, 2H), 3.59 (td, J = 4.9, 1.7 Hz, 2H), 3.51 (m, 6H), 3.49 (m, 6H), 3.43 (m, 2H), 3.38 (t, J = 6.4 Hz, 2H), 3.33 (t, J = 6.5 Hz, 2H), 1.33 (br s, 1800H). IR (KBr): ν_{max} 3448, 2919, 2850, 1474, 1138, 719 cm^{-1}. GPC analysis: $M_n = 10\,500$, M_w = 11 100, $M_p = 12\,100$, PDI = 1.06.

***ω*-Hydroxy-α-(1-pyrene-methyl ether) Polymethylene (25j).** 0.20 g (66%) of yellow solid. ^{1}H NMR (500 MHz, $CDCl_3$): δ 8.38 (d, 1H, J = 9.2 Hz), 8.19 (t, 2H, J = 7.0 Hz), 8.14 (m, 2H), 8.05 (s, 2H), 8.02 (m, 2H), 5.21 (s, 2H), 4.13 (q, 2H, J = 7.1 Hz), 3.61 (m, 2H), 1.67 (t, 2H, J = 7.2 Hz), 1.54 (m, 2H), 1.28 (s, 20 H). ^{13}C NMR (125 MHz, $CDCl_3$): δ 137.8, 131.8, 131.2, 130.8, 129.0, 128.6, 127.6, 127.4, 127.0, 126.9, 125.9, 125.1, 124.5, 123.5, 71.5, 70.6, 63.1, 32.8, 29.8, 29.7, 29.6, 29.4, 26.2, 25.7. IR (KBr): ν_{max} 3452, 3039, 2918, 2850, 1473, 1464 cm^{-1}. MALDI−TOF MS (AgTFA), M_p = *m/z* calcd for $C_{40}H_{58}O_2Ag$ $(M + Ag)^+$ 677.3, found 677.4. GPC analysis: M_n

= 310, $M_w = 340$, PDI = 1.10. Anal. Calcd for $C_{44}H_{66}O_2$: C, 84.28; H, 10.62. Found: C, 84.12; H, 10.66.

ω-Hydroxy-α-(*N*-benzylamino)polymethylene (25K). 66 mg (85%) of polymer. ^{1}H NMR (500 MHz, toluene-d_8): δ 7.60−7.51 (m, 2H), 7.14−7.09 (m, 3H), 3.79 (br s, 2H), 3.37 (t, J = 5.0 Hz, 2H), 2.49 (br s, 2H), 1.34 (s, 107H). IR (KBr): ν_{max} 3422, 2918, 2850, 1473 cm^{-1}. MS (ESI) $M_p = m/z$ calcd for $C_{59}H_{103}NO_2Na$ $(M + Na)^+$ 881; found 881; PDI = 1.08.

ω-Hydroxy-α-aminopolylmethylene (25l). A solution of 1.0 M $BH_3{\cdot}Me_2S$ (0.34 mL, 0.34 mmol) in CH_2Cl_2 was added to a solution of silylamine (0.4 g, 1.4 mmol) in THF (2 mL) and stirred 4 h at 40 °C. An aliquot of this solution (0.4 mL, 0.060 mmol) was added to a solution of ylide (0.66 M in toluene, 20.5 mL, 12.5 mmol) at 60 °C for 10 min. The solution was cooled to room temperature, and aqueous solutions of NaOH (0.4 mL, 2.40 mmol) and H_2O_2 (8.3 M, 0.40 mL, 3.3 mmol) were added and stirred 2 h at 40 °C. The polymer was precipitated by addition of acetonitrile (125 mL), filtered, washed with acetone, Et_2O, and hexanes (50 mL each), and dried in a vacuum oven (70 °C, 25 mmHg) for 20 h. The polymer was dissolved in toluene (3 mL), and aqueous HCl (1.0 mL, 2.9 mmol) was added and heated to 70 °C for 3 h. The solution was cooled, and the polymer precipitated by addition of acetonitrile (125 mL), filtered, and washed with aqueous $NaHCO_3$, H_2O, Et_2O, and hexanes (50 mL each). The polymer was dried in a vacuum oven (70 °C, 25 mmHg) for 20 h to afford a white polymer (165 mg, 81%). ^{1}H NMR (500 MHz, toluene-d_8, 90 °C): δ 3.38 (t, J = 6.5 Hz, 2H), 2.53 (t, J = 6.7 Hz, 2H), 1.34 (s, 218H). IR (KBr): ν_{max} 3448, 2918, 2850, 1473 cm^{-1}.

Acknowledgment. This work has been supported by a grant from the Chemistry Division (CHE-9617475) of the National Sciences Foundation.

Supporting Information Available: Synthesis and analytical data for functional olefin precursors **2**−**9**. This material is available free of charge via the Internet at http://pubs.acs.org.

References and Notes

(1) Zhang, Z.; Ying, S.; Hu, Q.; Xu, X. *J. Appl. Polym. Sci.* **2002**, *83*, 2625.
(2) Sriram, V.; Subramani, S.; Radhakrishnan, G. *Polym. Int.* **2001**, *50*, 1124.
(3) Du, J.; Peng, Y.; Zhang, T.; Ding, X.; Zheng, Z. *J. Appl. Polym. Sci.* **2002**, *83*, 1678.
(4) Sekkar, V.; Venkatachalam, S.; Ninan, K. *Eur. Polym. J.* **2002**, *38*, 169.
(5) Tsukahara, Y.; Ismail, H.; Takenaka, K.; Yoshimoto, N.; Kaeriyama, K. *Polym. Int.* **1999**, *48*, 398.
(6) Vlassopoulos, D.; Pitsikalis, M.; Hadjichristidis, N. *Macromolecules* **2000**, *33*, 9740.
(7) Martuscelli, E.; Musto, P.; Ragosta, G.; Riva, F.; Mascia, L. *J. Mater. Sci.* **2000**, *35*, 3719.
(8) Wagener, K.; Batich, C.; Kirsch, B.; Wanigatunga, S. *J. Polym. Sci., Part A: Polym. Chem.* **1989**, *27*, 2625.
(9) Tonelli, C.; Gavezotti, P.; Strepparola, E. *J. Fluorine Chem.* **1999**, *95*, 51.
(10) Dubois, P.; Jerome, R.; Teyssie, P. *Mater. Sci. Technol.* **1999**, *20*, 195.
(11) Hong, K.; Uhrig, D.; Mays, J. W. *Curr. Opin. Solid State Mater. Sci.* **1999**, *4*, 531.
(12) Bisht, H. S.; Chatterjee, A. K. *J. Macromol. Sci., Polym. Rev.* **2001**, *C41*, 139.
(13) Matyjaszewski, K. *Chem. Rev.* **2001**, *101*, 2921.
(14) Korolev, G. V.; Marchenko, A. P. *Russ. Chem. Rev.* **2000**, *69*, 409.
(15) Stridsberg, K. M.; Ryner, M.; Albertsson, A.-C. *Adv. Polym. Sci.* **2002**, *157*, 41.
(16) Agarwal, S.; Mast, C.; Dehnicke, K.; Greiner, A. *Macromol. Rapid Commun.* **2000**, *21*, 1952.
(17) Xudong, L.; Detrembleur, C.; Robert, J. *Macromolecules* **2002**, *35*, 1190.
(18) Hashimoto, K. *Prog. Polym. Sci.* **2000**, *25*, 1411.
(19) Grubbs, R. H.; Khosravi, E. *Mater. Sci. Technol.* **1999**, *20*, 65.
(20) Buchmeiser, M. R. *Chem. Rev.* **2000**, *100*, 1565.
(21) Piotti, M. E. *Curr. Opin. Solid State Mater. Sci.* **1999**, *4*, 539.
(22) Podesva, J.; Holler, P. *J. Appl. Polym. Sci.* **1999**, *74*, 3203.
(23) Jang, Y.-C.; Kim, P.-J.; Kwag, G.-H.; Kim, A.; Lee, S.-H. US Pat. Appl. Publ., US 20020016423, 2002.
(24) Pradel, J. L.; Boutevin, B.; Ameduri, B. *J. Polym. Sci., Part A: Polym. Chem.* **2000**, *34*, 7034.
(25) Fernyhough, C. M.; Young, R. N. *Macromolecules* **2001**, *34*, 7034.
(26) Grubbs, R. H.; Morita, T.; Maughon, B. R.; Bielawski, C. W. *Macromolecules* **2000**, *33*, 6621.
(27) Brookhart, M.; Desimone, J. M.; Grant, B. E.; Tanner, M. J. *Macromolecules* **1995**, *28*, 5378.
(28) Shea, K. J.; Zhu, H.; Walker, J. R.; Paz, M. M.; Greaves, J. *J. Am. Chem. Soc.* **1997**, *119*, 9049.
(29) Shea, K. J.; Busch, B. B.; Paz, M. M. *Angew. Chem., Int. Ed. Engl.* **1998**, *38*, 1391.
(30) Shea, K. J.; Lee, S. Y.; Busch, B. B. *J. Org. Chem.* **1998**, *63*, 5746.
(31) Shea, K. J. *Chem. Eur. J.* **2000**, *6*, 1113.
(32) Shea, K. J.; Wagner, C. E. *Org. Lett.* **2001**, *3*, 3063.
(33) Shea, K. J.; Busch, B. B.; Paz, M. M.; Staiger, C. L.; Stoddard, J. M.; Walker, J. R.; Zhou, X.; Zhu, H. *J. Am. Chem. Soc.* **2002**, *124*, 3636.
(34) Shea, K. J.; Zhou, X.-Z. *J. Am. Chem. Soc.* **2000**, *122*, 11515.
(35) Brown, H. C. *Organic Synthesis via Boranes*; Wiley-Interscience: New York, 1975.
(36) Pelter, A.; Smith, K.; Brown, H. C. *Borane Reagents*; Academic Press: New York, 1988.
(37) Thomas, S. E. *Organic Synthesis: The Role of Boron and Silicon*; Oxford University Press: New York, 1994.
(38) Matteson, D. S. *Stereodirected Synthesis with Organoboranes*; Springer-Verlag: Berlin, 1995.
(39) Bergbreiter, D.; Gray, H. N.; Srinivas, B. *Macromolecules* **1994**, *27*, 7294.
(40) Jerabek, K.; Shea, K. J.; Sasaki, D. Y.; Stoddard, G. J. *J. Polym. Sci., Part A: Polym. Chem.* **1992**, *30*, 605.
(41) Ivanov, V. B.; Behnisch, J.; Hollaender, A.; Mehdorn, F.; Zimmermann, H. *Surf. Interface Anal.* **1996**, *24*, 257.
(42) Aplin, J. D.; Hughes, R. C. *Anal. Biochem.* **1981**, *113*, 144.
(43) Singhvi, R.; Kumar, A.; Lopez, G. P.; Stephanopoulos, G. N.; Wang, D. I.; Whitesides, G. M.; Ingber, D. E. *Science* **1994**, *264*, 696.
(44) Sundberg, S. A.; Barrett, R. W.; Pirrung, M.; Lu, A. L.; Kiangsoontra, B.; Holmes, C. P. *J. Am. Chem. Soc.* **1995**, *117*, 12050.
(45) Mrksich, M.; Whitesides, G. M. *Annu. Rev. Biophys. Biomol. Struct.* **1996**, *25*, 55.
(46) Gough, A. H.; Jung, D. R.; Taylor, D. L. PCT Int. Appl., WO 0017624, 1999.
(47) Bruening, R. L.; Krakowiak, K. E. PCT Int. Appl., WO 0076616, 2000.
(48) Novaimi, M.; Moschel, K.; Bisswanger, H. *Enzyme Microbial Technol.* **2001**, *29*, 567.
(49) Xue, H.; Bhowmik, P.; Schlick, S. *Macromolecules* **1993**, *26*, 3340.
(50) Xue, H.; Xu, S.; Bhowmik, P.; Schlick, S. *Macromolecules* **1995**, *28*, 3351.
(51) Xu, J.; Dimonie, V.; Sudol, E.; Klein, A.; El-Aasser, M. *J. Appl. Polym. Sci.* **1998**, *69*, 985.
(52) Xu, J.; Dimonie, V.; Sudol, E.; Shaffer, O.; El-Aasser, M. *J. Appl. Polym. Sci.* **1998**, *69*, 977.
(53) Xu, J.; Dimonie, V.; Sudol, E.; El-Aasser, M. *J. Appl. Polym. Sci.* **1998**, *69*, 965.
(54) Takasu, M.; Yamamoto, H. *Synlett* **1990**, *4*, 1946.
(55) Bertozzi, C. R.; Bednarski, M. D. *J. Org. Chem.* **1991**, *56*, 4326.
(56) Ruyter, C. M.; Stockigt, J. H. *Helv. Chim. Acta* **1991**, *74*, 1703.
(57) Cruz, A.; Geniz, E.; Contreras, R. *Tetrahedron: Asymmetry* **1998**, *9*, 3991.
(58) Hosomi, A.; Sakata, Y.; Sakarai, H. *Tet. Lett.* **1984**, *25*, 2383.
(59) Potter, B. V.; Marwood, R. D.; Riley, A. M.; Jenkins, D. J. *J. Chem. Soc., Perkin Trans. 1* **2000**, *12*, 1935.
(60) Kabalka, G. W.; Li, N. S.; Pace, R. D. *Synth. Commun.* **1995**, *25*, 2135.
(61) Overman, L.; Okazaki, M.; Mishra, P. *Tetrahedron Lett.* **1986**, *47*, 4391.
(62) Benmaarouf-Khallaayoun, Z.; Baboulene, M.; Speziale, V.; Lattes *Phosphorus Sulfur* **1998**, *36*, 181.
(63) Brown, H. C. *Hydroboration*; Benjamin: New York, 1962.
(64) Onak, T. *Organoborane Chemistry*; Academic Press: New York, 1975.

(65) Brown, H. C.; Chandrasekharan, J. *J. Org. Chem.* **1988**, *53*, 4811.
(66) Belu, A. M.; Desimone, J. M.; Linton, R. W.; Lange, G. W.; Friedman, R. M. *J. Am. Soc. Mass Spectrom.* **1996**, *7*, 11.
(67) Bauer, B. J.; Wallace, W. E.; Fanconi, B. M.; Guttman, C. M. *J. Am. Soc. Mass Spectrom.* **2001**, 1186.
(68) Chen, R.; Li, L. *J. Am. Soc. Mass Spectrom.* **2001**, *12*, 367.
(69) Kahr, M. S.; Wilkins, C. L. *J. Am. Soc. Mass Spectrom.* **1993**, *12*, 367.
(70) We have not yet analyzed trimethylsilyl, tri-*n*-butyltin, biotin, mannose, pegalated dansyl, and pegalated pyrene by MALDI-TOF.

MA020729N