ACCOUNTS
of chemical research

Polyhomologation. A Living C1 Polymerization

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RECEIVED ON APRIL 14, 2010

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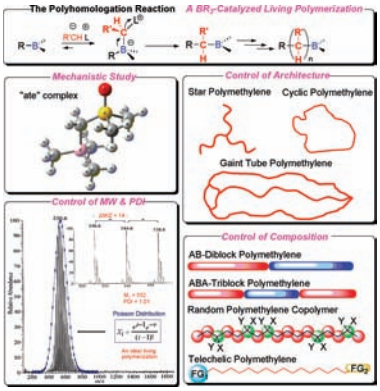

The physical properties of synthetic macromolecules are strongly coupled to their molecular weight (MW), topology, and polydispersity index (PDI). Factors that contribute to their utility include the control of functionality at the macromolecule termini and copolymer composition. Conventional polymerization reactions that produce carbon backbone polymers (ionic, free radical, and coordination) provide little opportunity for controlling these variables. Living polymerizations, sometimes referred to as controlled polymerizations, have provided the means for achieving these goals. Not surprisingly, these reactions have had a profound impact on polymer and materials science.

Three basic reaction types are used for the synthesis of most carbon backbone polymers. The first examples of "living" polymerizations were developed for ionic polymerizations (cationic and anionic). These reactions, which can be technically challenging to perform, can yield excellent control of molecular weight with very low polydispersity. The second reaction type, free radical polymerization, is one of the most widely used polymerizations for the commercial production of high molecular weight carbon backbone polymers. Nitroxide mediated polymerization (NMP), reversible addition−fragmentation chain transfer polymerization (RAFT), and atom transfer radical polymerization (ATRP) have emerged as three of the more successful approaches for controlling these reactions. The third type, transition metal mediated coordination polymerization, is the most important method for large-scale commercial polyolefin production.

Simple nonfunctional hydrocarbon polymers such as polyethylene (PE), polypropylene, poly-α-olefins, and their copolymers are synthesized by high pressure-high temperature free radical polymerization, Ziegler−Natta or metallocene catalysts. Although these catalysts of exceptional efficiency that produce polymers on a huge scale are in common use, control that approaches a "living polymerization" is rare. Although the controlled synthesis of linear "polyethylene" described in this Account is not competitive with existing commercial processes for bulk polymer production, they can provide quantities of specialized materials for the study of structure−property relationships. This information can guide the production of polymers for new commercial applications.

We initiated a search for novel polymerization reactions that would produce simple hydrocarbon polymers with the potential for molecular weight and topological control. Our research focused on polymerization reactions that employ nonolefin monomers, more specifically the polymerization of ylides and diazoalkanes. In this reaction, the carbon backbone is built one carbon at a time (C1 polymerization). These studies draw upon earlier investigations of the Lewis acid catalyzed polymerization of diazoalkanes and build upon our discovery of the trialkylborane initiated living polymerization of dimethylsulfoxonium methylide **1**.

1. Introduction

The annual worldwide production of polyethylene (PE) is over 79 million tons.[1] The majority of commercial PE is prepared by traditional polymerization methods.[2] These methods result in PE with a spectrum of physical properties, which, together with its low cost, processability, and recyclability, provides for applications that range from commodity packaging to precision mechanical material (artificial joint replacements).[3] PE is ubiquitous in contemporary society.

The low cost and malleable physical properties of PE motivate efforts to extend its use to products of high value. However, it is PE's physical

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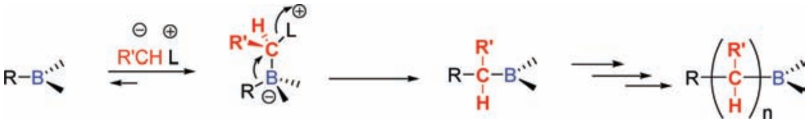
10.1021/ar100062a

SCHEME 1. General Illustration for Organoborane Catalyzed/Initiated C1 Polymerization



properties and methods of production that contribute to limiting realization of this goal. The industrial ethylene polymerization methods are not well suited for fine control of polymer architecture or molecular weight, and relatively few methods satisfy the criteria for a living olefin polymerization.[3−5]

In this Account, we describe the polyhomologation reaction, a living polymerization that results in the synthesis of linear polymethylene with no branches, controlled molecular weight, narrow molecular weight distribution, well-defined topology and composition. Polymethylene is a unique member of the polyethylene family. The carbon backbone is built one carbon at a time in contrast to two carbons in ethylene polymerization.[6,7] In addition, since many vinyl compounds do not readily polymerize, the polyhomologation reaction can serve as an entry to completely new substances.

The general reaction involves formation of an organoboron "ate" complex between an ylide and a Lewis acidic borane (Scheme 1).[8] The "ate" complex breaks down by an intramolecular 1,2-migration. This step results in formation of a new sp^3-sp^3 carbon−carbon bond and extends by one carbon the alkyl chain. This step also regenerates the Lewis acid site. Repetition of this process yields a perfectly linear hydrocarbon chain. The boron catalyzed/initiated polymerization of ylides is a controlled synthesis of linear polymethylene (PM), a surrogate for PE.

2. A Living Polymerization of Ylides

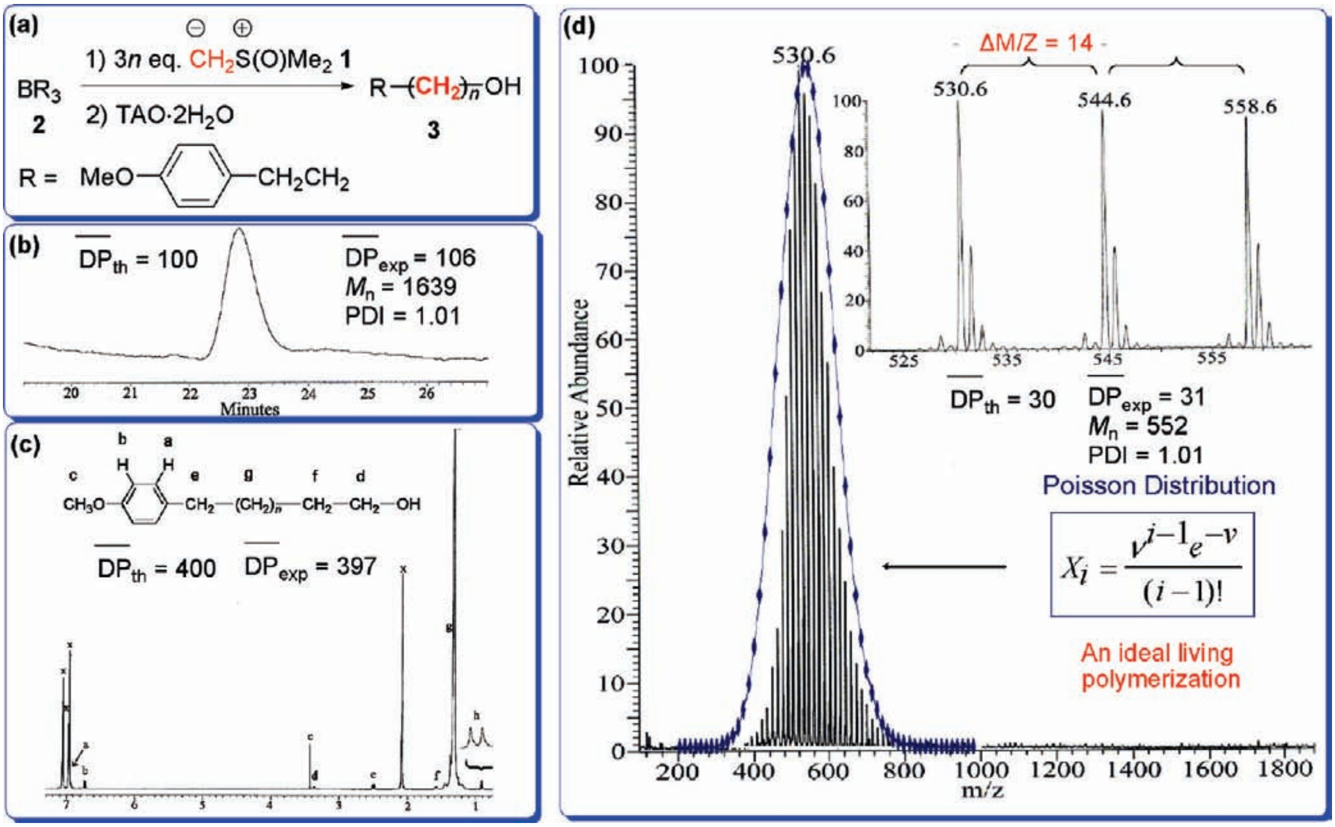
Controlled synthesis of linear hydrocarbon polymers has been achieved by the Lewis acid catalyzed/initiated polymerization of ylides and ylide-like monomers. Dimethylsulfoxonium methylide **1** has been the most common monomer used for these polymerizations.[8] Dimethylsulfoxonium methylide **1**, an ylide developed by Corey and co-worker, is prepared by the deprotonation of trimethylsulfoxonium chloride with sodium hydride.[9]

In a representative polyhomologation reaction, a solution of tris(4-methoxyphenylethyl)borane **2** (1 equiv) was rapidly injected into a solution of ylide **1** [300 equiv, theoretical average degree of polymerization ($\overline{DP}_{th}$) = 100] in toluene preheated to 70 °C (Figure 1a). Ylide **1** was consumed within 10 min. The cooled solution was treated with trimethylamine *N*-oxide dihydrate ($TAO \cdot 2H_2O$), and the resulting polymer was isolated by precipitation to afford α-hydroxy-*ω*-(4-methoxyphenyl)polymethylene **3** in yields ranging from 85 to 95%.[10] α-Hydroxy-*ω*-(4-methoxyphenyl)polymethylene **3** was synthesized with a wide range of $\overline{DP}$. Molecular weight analyses established a correlation between the theoretical and observed molecular weights, a result consistent with a living polymerization (Figure 1). Low polydispersities (1.01−1.04) further support the living character of the reaction. A typical ^{1}H NMR spectrum of polymethylene **3** confirms the linear structure with hydroxyl and 4-methoxyphenyl groups at each termini of the polymer chain (Figure 1c).

A representative field desorption mass spectrometry (FDMS) spectra of polymethylene **3** shows a monomodel distribution of peaks separated by 14 amu (Figure 1d).[10] This polymethylene "signature" confirms that the reaction builds the polymethylene chain one carbon at a time with $-CH_2-$ repeating units. The dark blue curve in Figure 1d is a simulated distribution of polymer produced by an ideal living polymerization generated by a Poisson distribution function.[11] The near superimposition of the experimental and calculated polymer distributions is compelling support for the almost "perfect" living nature of the polyhomologation reaction.

A representative gel permeation chromatography (GPC) of polymethylene **3** shows a narrow, monodisperse polymer distribution with experimental average degree of polymerization $\overline{DP}_{exp}$ in agreement with the calculated molar ratio of [ylide]/3[BR_3] (Figure 1b).[10] The stoichiometry of the reaction between ylide **1** (3*n* equiv) and tris(4-methoxyphenylethyl)borane **2** (1 equiv) is consistent with the formation of an intermediate three-arm star polymethylene **4** ($\overline{DP} = 3n$) (Scheme 2). Oxidation of star polymethylene **4** affords 3 equiv of α-hydroxy-*ω*-(4-methoxyphenyl)polymethylene **3** with $\overline{DP} = n$.[8] The strict correspondence between stoichiometry and $\overline{DP}$ in these examples is consistent with a rapid initiation and the absence of termination or chain transfer reactions in the polymerization of ylide **1**.

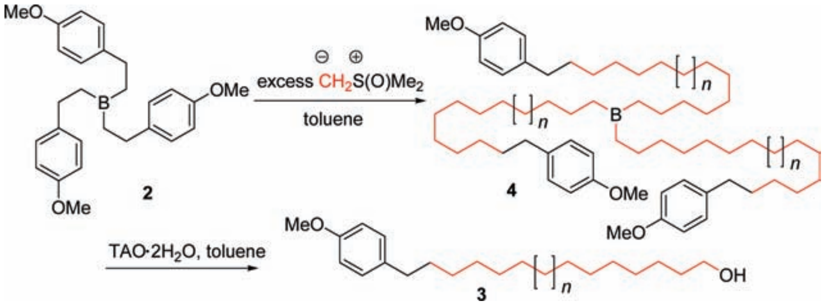
The absence of a termination step during the polyhomologation reaction was demonstrated by the synthesis of α-hydroxy-*ω*-(4-methoxyphenyl)polymethylene-*co*-polyperdeuteriomethylene (Scheme 3).[8] The copolymer was prepared by the addition of tris(4-methoxyphenylethyl)borane **2** to a toluene solution of ylide **1**. After ylide **1** consumption, a solution



$$X_i = \frac{\nu^{i-1} e^{-\nu}}{(i-1)!}$$

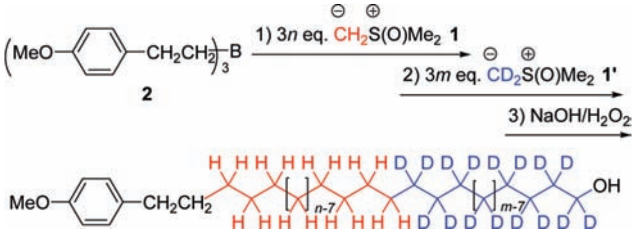
FIGURE 1. (a) Synthesis of α-hydroxy-ω-(4-methoxyphenyl)polymethylene **3**. (b) Typical GPC of α-hydroxy-ω-(4-methoxyphenyl)-polymethylene **3**. (c) 500 MHz ^{1}H NMR (x: toluene-d_8) of α-hydroxy-ω-(4-methoxyphenyl)polymethylene **3**. (d) Representative FDMS spectrum of α-hydroxy-ω-(4-methoxyphenyl)polymethylene **3**. Inset shows an expanded scale revealing isotope patterns with each main peak separated by 14 *m*/*e*. The dark blue curve is a plot of the simulated distribution of a theoretical polymer of comparable molecular weight produced by an ideal living polymerization. The plot is generated by a Poisson distribution function.

SCHEME 2. Tris(4-methoxyphenylethyl)borane **2** Initiated Polyhomologation of Ylide **1** Produces an Intermediate Three-Arm Star Polymethylene **4**; Oxidation of the Carbon−Boron Bonds Affords Linear α-Hydroxy-ω-(4-methoxyphenyl)polymethylene **3**

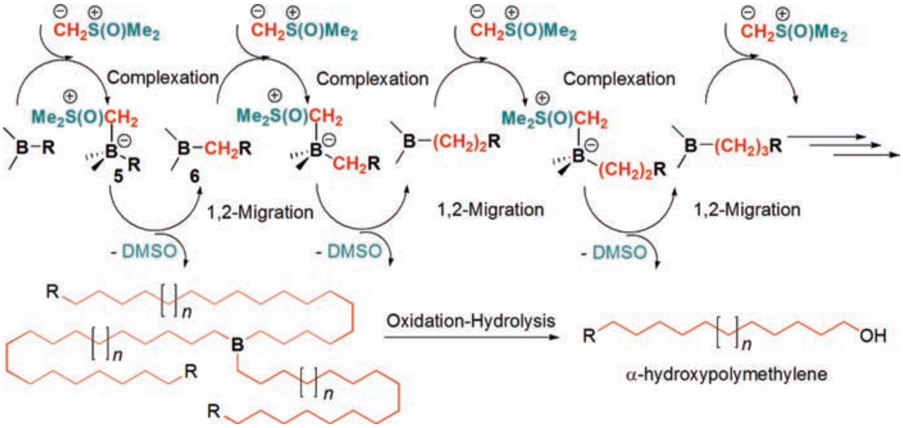


of *perdeuterio* ylide **1′** was added. Subsequent oxidation produced the linear terminal alcohol. FDMS analysis reveals a distribution of molecular ions consistent with a copolymer of α-hydroxy-ω-(4-methoxyphenyl)polymethylene containing $(CH_2)_n(CD_2)_m$ units, where 3*n* and 3*m* represent the equivalents of *protio* ylide **1** and *perdeuterio* ylide **1′** added, respectively. The ability to generate diblock polymers by chain-extension, the close agreement between experimental and calculated molecular weight distributions, and the narrow

SCHEME 3. Synthesis of α-Hydroxy-ω-(4-methoxyphenyl)-polymethylene-*co*-polyperdeuteriomethylene



SCHEME 4. Proposed Mechanism for the Polyhomologation Reaction



polydispersities provide compelling support for the living nature of the polyhomologation reaction.

The polyhomologation reaction has been used to prepare polymethylene with a M_n as high as 354 KDa corresponding to an intermediate tris(polymethylene)borane with $M_n > 1.0 \times 10^6$. The reaction is complete in <10 min, from which one estimates a lower limit turnover frequency of 6.4×10^6 g of polymethylene (mol boron)$^{-1}$ h^{-1} at 120 °C, comparable to some of the most efficient homogeneous ethylene polymerization catalysts.[10]

3. Mechanism of the Polyhomologation Reaction

The proposed mechanism for the formation of polymethylene is shown in Scheme 4. The reaction is initiated by attack of the nucleophilic ylide **1** on the Lewis acidic trialkylborane to form a zwitterionic complex **5**, which subsequently undergoes a 1,2-migration of one of the three alkyl substituents on boron to the methylene group. This results in a homologated borane **6** and a molecule of dimethyl sulfoxide (DMSO). After each migration the Lewis acidic boron center is regenerated, permitting reaction with another ylide **1** monomer. Repetition of this affords a polymethylene chain.[12] The low polydispersity index (PDI) of these polymerizations implies that all three alkyl groups on boron undergo migration with equal probability resulting in the three polymethylene chains with the same average chain length.

The proposed mechanism was supported by a ^{11}B NMR study.[10] In noncoordinating solvents, there is a significant chemical shift difference between trialkylboranes (80−90 ppm) and tetraalkylborate complexes (−20 to −10 ppm).[13] The ^{11}B NMR spectrum of tri-*n*-hexylborane in toluene at 40 °C exhibits a single resonance at 87.4 ppm (Figure 2a). When an equimolar amount of ylide **1** was added at −78 °C followed by warming to −15 °C, the peak at 87.4 ppm disappeared and a new resonance was observed at −13.4 ppm (Figure 2b). The observation is consistent with quantitative formation of the zwitterionic complex **5** (Scheme 5). Warming the mixture to 40 °C results in conversion to a single resonance at 82.2 ppm (Figure 2c). The new signal is attributed to the homologated trialkylborane **6,** formed after 1,2-migration.

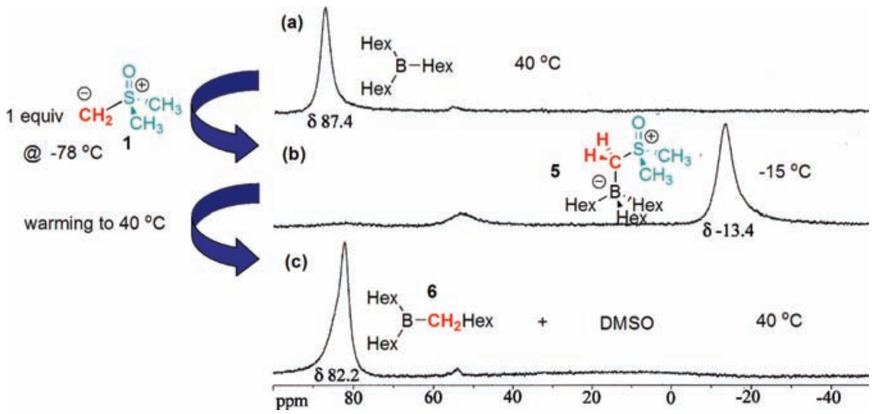
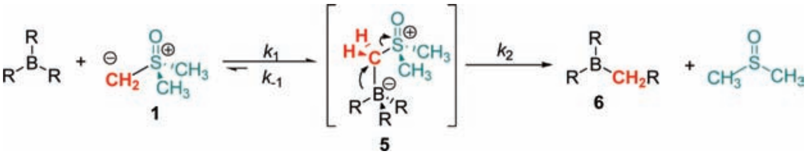


FIGURE 2. ^{11}B NMR of (a) tri-*n*-hexylborane (40 °C), (b) tri-*n*-hexylborane·ylide complex **5** (−15 °C), and (c) trialkylboranes **6** and DMSO product mixture (40 °C) in toluene. The small peak at 48 ppm is a borinic ester impurity (<2%).

SCHEME 5. Pre-Equilibrium Followed by a Rate-Limiting 1,2-Migration



(Note that the rate of the polyhomologation reaction at −15 °C is very slow.)

Based on the preceding ^{11}B NMR spectra, a pre-equilibrium exists between the borane initiator and ylide that strongly favors formation of the zwitterionic complex **5** (Scheme 5). The pre-equilibrium is established immediately, and complex **5** is stable at −15 °C. These results are consistent with the proposed mechanism of a rapid pre-equilibrium followed by a rate-limiting 1,2-migration step since homologation only proceeds at an appreciable rate at 40 °C.[10]

Additional support for a rate-limiting 1,2-migration step was obtained from kinetic studies.[10] Plots of the consumption of ylide **1** versus time are linear over more than 3 half-lives, indicating that accumulated DMSO does not inhibit the polyhomologation reaction. Under pseudo-first-order conditions, the reaction is first order in organoborane and zero order in ylide **1**, a result consistent with the proposed two-step mechanism (Scheme 5). The rate expression is d[product]/dt = rate = $k_2[R_3B\cdot \text{ylide}]$. When ylide **1** is in large excess, the concentration of complex **5** will be approximated by the initial trialkylborane concentration. The rate expression can be written as rate = $k_2[R_3B]_0$, consistent with the kinetic results.

The rate-determining step of the polyhomologation reaction is the 1,2-migration of an alkyl group from boron to carbon in the zwitterionic complex **5**. Structural analysis of zwitterionic ylide **1** complexes provides insight to the stereoelectronic requirements for the rearrangement.

The structure of ylide·BF_3 complex **7**, a stable surrogate for complex **5**, was obtained by single crystal X-ray analysis (Figure 3a).[14] The complex has a staggered conformation about the B1−C1 bond with an alignment of one of the boron−fluorine bonds *anti* to the carbon−sulfur bond (F1−B1−C1−S1 = −161.21°). The S1−O1 bond of complex **7** is aligned *anti* to the B1−C1 bond (B1−C1−S1−O1 = 166.42°), which can be attributed in part to the opposing dipole moments of the BF_3 and S−O groups. We suggest that this ground state conformation can be understood in terms of a stabilizing orbital interaction that aligns the migrating and leaving groups in zwitterionic complex **5**.

A computational study of the ground state of ylide·BMe_3 complex **8**, a surrogate for **5**, was obtained from a DFT/B3LYP/6-311G(d,p) calculation (Figure 3b).[15] The calculation positions the migrating alkyl group on boron *anti* to the sulfoxonium group, and the S−O bond of complex **8** is aligned *anti* to the B−C bond as well.

Both the X-ray diffraction structure and computational result reveal a trans *anti*-periplanar relationship between the migrating R−B bond and the C−S leaving group. These ground state structures (**7**, **8**) foreshadow the transition states for the 1,2-migration. The low energy conformation arises from a stabilizing interaction between the filled B−C σ orbital and the empty S−O σ^* orbital (Figure 4a). This would be optimal when the migrating group R is orientated *anti*-periplanar to the C−S leaving group. This orientation allows the filled

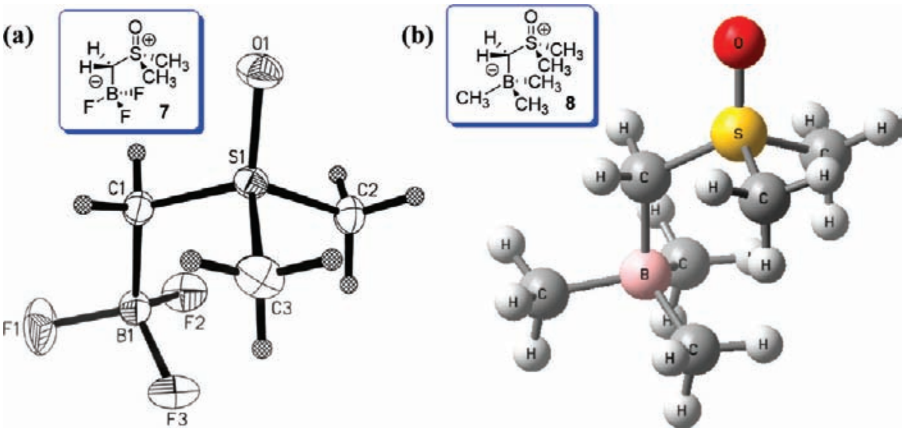


FIGURE 3. Molecular structure of (a) ylide·BF_3 complex **7** obtained from a single-crystal X-ray analysis and (b) ylide·BMe_3 complex **8** obtained from a DFT/B3LYP/6-311G(d,p) calculation.

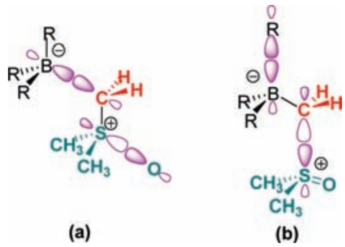
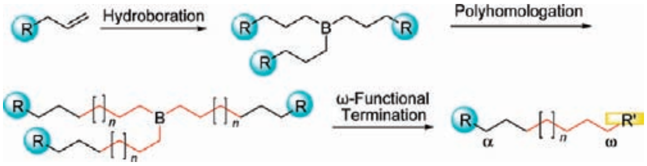


FIGURE 4. Proposed molecular orbital interactions of zwitterionic complex **5** deduced from X-ray and calculated ground state structures of **7** and **8**. (a) The filled B−C σ orbital aligns *anti*-periplanar to the empty S−O σ^* orbital for stabilization. (b) The migrating group (HOMO: C−B σ) aligns *anti*-periplanar to the sulfoxonium leaving group (LUMO: C−S σ^*) during 1,2-migration.

SCHEME 6. Synthetic Strategy of Telechelic Polymethylene



R−B σ orbital (HOMO) to interact with the unfilled C−S σ^* orbital (LUMO) during 1,2-migration (Figure 4b).[14] The *anti*-periplanar relationship between migrating and leaving groups has been observed in related 1,2-migrations.[16−20]

4. Telechelic Polymethylene

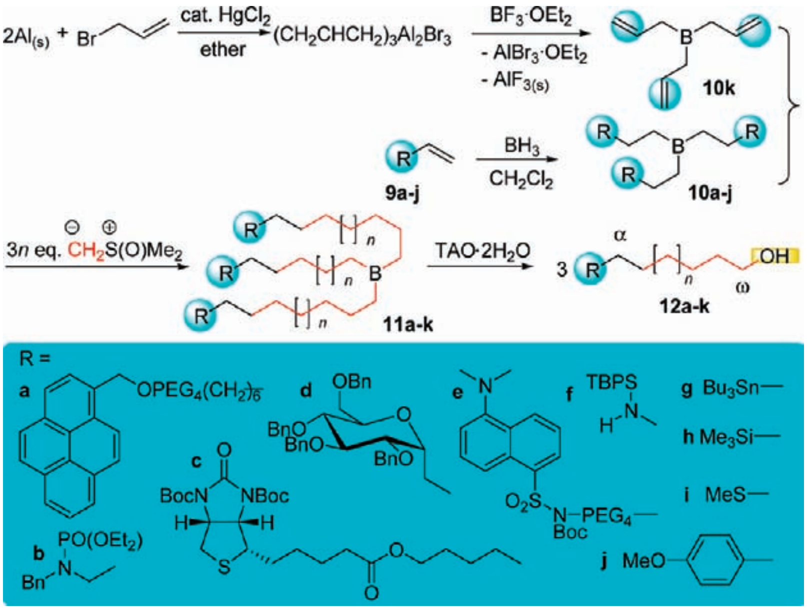
The polyhomologation reaction can be used to prepare telechelic polymethylenes. The α- and ω-positions of the polymethylene chain may be differentially functionalized by (1) the use of a functional trialkylborane initiator/catalyst or (2) subsequent chemical transformations of the resulting three-arm star polymethylene borane (Scheme 6).

4.1. α-Termini Functionality from a Functionalized Organoborane Initiator/Catalyst. Functionality at the α-chain end arises from the substituents on the trialkylborane initiator/catalytst which can be prepared by hydroboration of functional α-olefins (**10a**−**j**) or by direct synthesis (**10k**) (Scheme 7).[21,22] ω-Hydroxy polymethylenes **12a**−**k** were prepared by a polyhomologation−oxidation sequence. Both ^{1}H NMR and GPC confirmed quantitative incorporation of functional groups on each end of the linear polymer chain. All polymers displayed monomodal GPC profiles with PDIs that ranged from 1.01 to 1.19.

For low molecular weight telechelic polymethylene (MW < 2000), polar functionality or aromatic rings facilitate the ionization and desorption of molecular ions during the analyses of MALDI-TOF or electrospray ionization mass spectrometry (ESI-MS).[21] For example, α-benzylamino-ω-hydroxyl polymethylene, produced from deprotection of telechelic polymethylene **12b**, shows a near Poisson distribution (PDI ∼ 1.07) of $(M + Na)^+$ ions from ESI-MS analysis (Figure 5).

4.2. ω-Termini Functionality from the Chemical Transformation of Tris(Polymethylene)Organoboranes. Functional groups can also be incorporated onto the ω-position of polymethylene *after* polymerization. The primary products of the polyhomologation reaction (tris(polymethylene)organoboranes) are amenable to a number of synthetic transformations that replace boron with another functionality, including hydroxyl, hydrogen (alkanes), amines, halogens, and carbon−metal

SCHEME 7. Synthesis of ω-Hydroxypolymethylenes **12a**−**k** from Functional Trialkylboranes



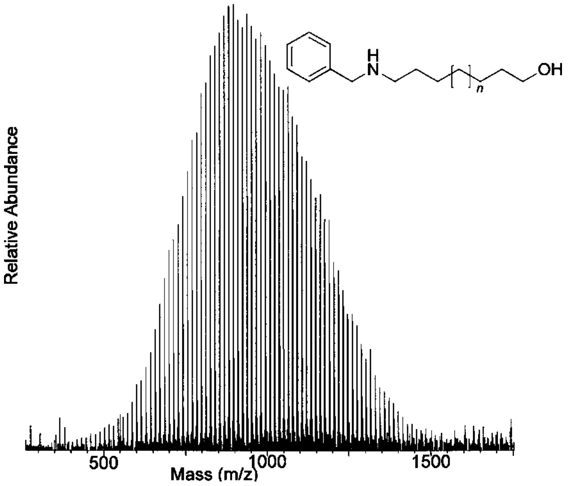


FIGURE 5. ESI-MS mass spectrum of α-benzylamino-ω-hydroxyl polymethylene $(M + Na)^+$. $M_n = 942$, $M_w = 1,006$, PDI = 1.07.

bonds.[13] For example, triallylborane **10k** was used as a vinyl-functionalized organoborane initiator to produce organoborane intermediate **11k**. Protolysis of this intermediate **11k** with propionic acid yielded α-vinyl-ω-methylpolymethylene.[22]

5. Topological Control of Polymenthylene

For polymers with identical chemical composition and similar molecular weight, topology can be used to alter physical properties including density, crystallinity, diffusion rate, melt rheology, and mechanical strength.[3,23−25] Ethylene polymerization presents significant challenges to precisely control architecture. Examples include cyclic polyethylene synthesized by ring-opening metathesis polymerization (PDI of 2), star, comb, H-shape, and pom-pom polyethylenes produced by anionic polymerization (with ethyl branching defects).[23,24]

Post-polymerization modification of PM and the use of structurally novel borane initiators provide an opportunity to control polymer topology. Examples including three-arm star polymers, giant tubelike structures, and macrocycles are illustrated below.

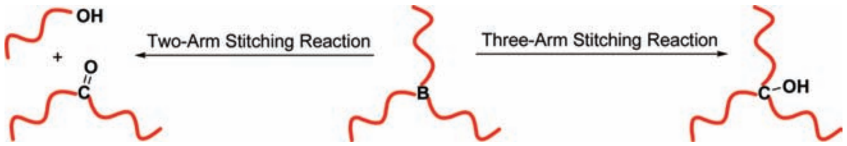
5.1. Post-Polymerization Control of Topology. There are standard protocols for converting trialkylboranes to a diverse number of architectures (Scheme 8).[13] For example, trialkylboranes can undergo "three-arm stitching" to join the three alkyl groups on boron to a common carbon atom. Alternatively, a "two-arm stitching" reaction can form a symmetrical linear ketone. These transformations can be used following polyhomologation to assemble novel polymethylene structures incorporating terminal functionality that can be used for further modification.

For example, following polyhomologation of tris(4-methoxyphenylethyl)borane **2**, tris(polymethylene)borane was treated with α,α-dichloromethyl methyl ether and base. Oxidation afforded a three-arm star polymer, tris(polymethylene)carbinol **13** (Scheme 9).[26] These three-arm star polymethylene architectures are prepared with well-controlled molecular weight and low PDI. Functional groups can be installed at all three termini of the star polymethylene by using trifunctionalized borane initiator/catalyst BR_3.

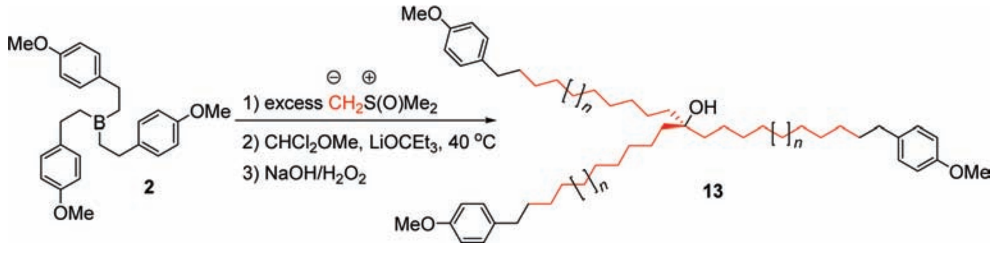
5.2. Initiator-Based Topological Control. Structurally novel borane initiators can also provide access to well-defined polymethylene architectures. For example, the polyhomologation reaction of 1-boraadamantane·THF **14** with ylide **1** produced a "tubelike" macropolycylcic organoborane **15**, which upon oxidation gave a regular A_3 three-arm star polymethylene **16** (Scheme 10).[18,27] Both ^1H NMR and GPC (triple detector) analyses of the product **16** confirm the regular A_3 star architecture. This implies all three branches of the propagating species participate in migration with equal probability.

Interestingly, $\overline{DP}_{exp}$ of star polymer **16** was consistently *three times* greater than $\overline{DP}_{th}$, despite the fact that the PDIs of

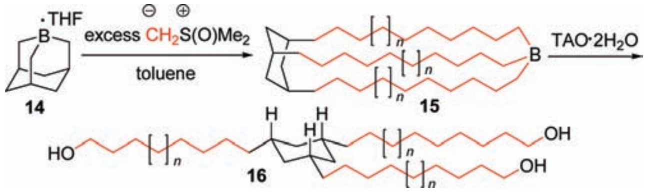
SCHEME 8. Illustration of Two-Arm and Three-Arm Stitching Reactions



SCHEME 9. Synthesis of Tris(polymethylene)carbinol **13** from Tris(4-methoxyphenylethyl)borane **2**



SCHEME 10. Synthesis of Three-Arm Star Polymethylene Polymer **16** Incorporating a *cis,cis*-1,3,5-Trisubstituted Cyclohexane Core from 1-Boraadamantane·THF **14**



star polymers **16** are <1.12.[18] It was found that approximately two-thirds of the propagating species become "trapped" during the early stages of the polyhomologation reaction and do not proceed to form high molecular weight polymer. During initial insertion of methylenes into the three branches of the tricyclic organoborane, the reaction diverges from a "single-site" catalyst to one with multiple reaction sites, two-thirds of which are nonproductive. The nonproductive centers arise during the early stages of expansion of the polycyclic rings. These species are isomeric caged tricyclic structures with *inverted* pyramidal boron centers with high activation energies for addition of monomer (Figure 6). However, at least one intermediate, after approximately six insertions, can proceed rapidly to give polymer with a molecular weight three times greater than calculated. After overcoming the pitfalls of the *initial stages* of polymerization, the polycyclic boranes are expanded to large rings, and each branch migrates with equal probability in a manner similar to acyclic alkylborane. Despite the mechanistic complication, the reaction produces regular A_3 three-arm star polymers with MW of $\sim$20 000 and PDI of 1.08.

5.3. Topological Control from a Combination of Initiator and Post-Polymerization Modification. Other novel polymethylene architectures can be obtained by related "stitching" reactions of polyhomologated organoboranes produced from cyclic initiators. For example, the construction of macrocyclic polymethylene is achieved by "two-arm stitching" of a side chain-blocked boracyclane initiator (Scheme 11). If a blocking group occupies the side chain position on a boracyclane, that is, **19**, polyhomologation results in exclusive ring expansion to produce a macrocyclic ring **20**. The subsequent stitching joins the two branches to construct the macrocarbocyclic polymer **21**.

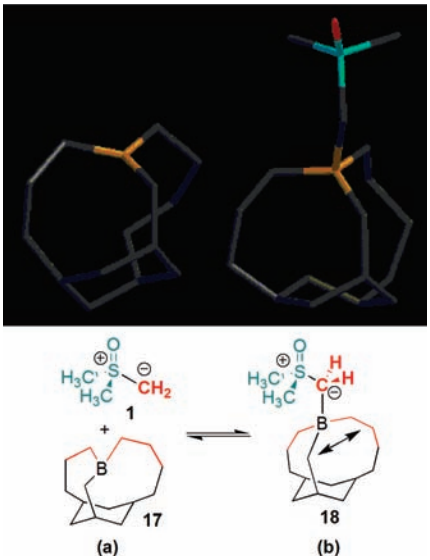
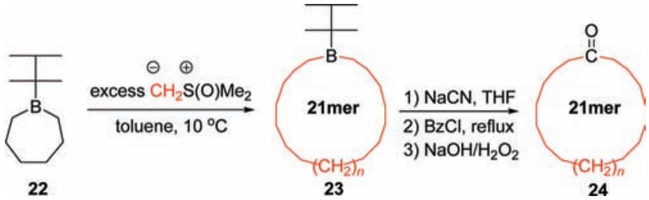


FIGURE 6. Computational results of the [3.2.0] system **17** and its complex **18**. (a) Several tricyclic boranes at the fourth through sixth homologated stages contain *inverted* pyramidalized boron centers that arise to reduce transannular interactions and angle strain. (b) Complex formation of the ylide **1** with the inverted carboranes is endothermic, reducing the rate of homologation.

SCHEME 12. Synthesis of Oligomeric Cyclic Ketone **24** from *B*-Thexylborocane **22**

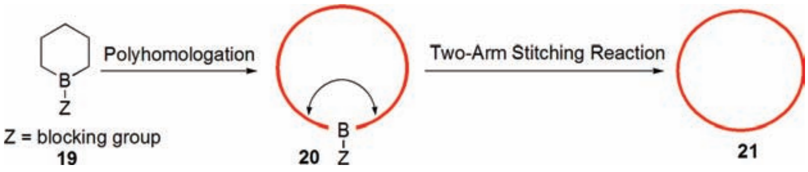


In one example, the thexyl group, a substituent with known low migratory aptitude, was employed as a blocking group.[17] Polyhomologation of *B*-thexylborocane **22** at 5−10 °C gave boracycle **23** which was treated with sodium cyanide and benzyl chloride then oxidatized to produce a Poisson distribution of cyclic ketones **24** (Scheme 12).[28]

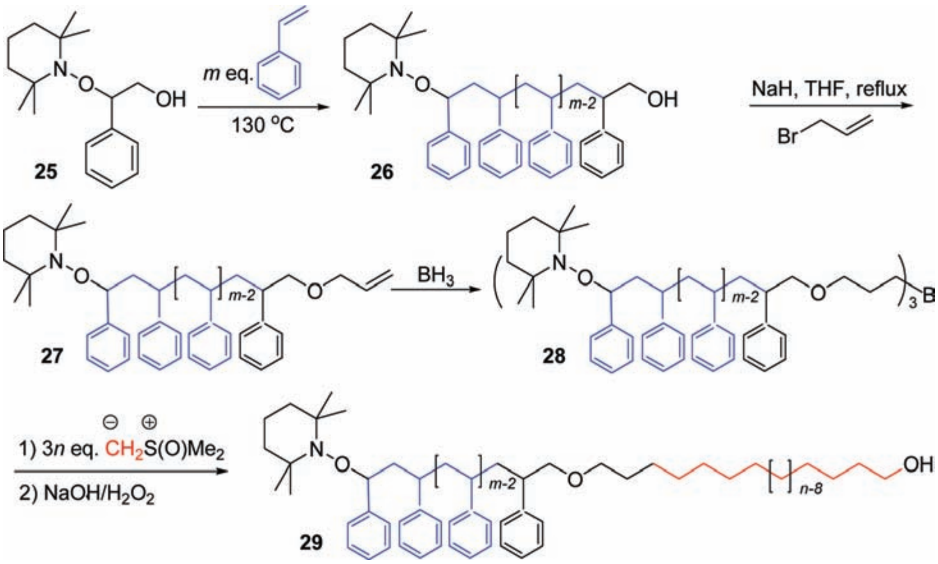
6. Copolymers of Polymethylene

Despite the widespread use of polyethylene, nonpolarity and the high degree of crystallinity impart polyethylene with poor adhesion properties, incompatibility with many materials and

SCHEME 11. Illustration of the Synthesis of Macrocyclic Polymethylene **21** from a Side Chain-Blocked Boracyclane Initiator **19** Followed by "Two-Arm Stitching" Reaction



SCHEME 13. Procedure for the Synthesis of Poly(methylene-*b*-styrene) **29**



thus prevent its wider use. One approach to extend the application of polyethylene is to incorporate polyethylene segments in block copolymers.

The properties of polyethylene block copolymers depend on the structural and compositional parameters including the distribution and relative amounts of each segment, the molecular weight and PDI of each segment.[29] This is best achieved by the introduction of each block in a controlled manner. Since the polyhomologation reaction provides accurate control of the polymethylene segments, it can be combined with other controlled polymerization reactions for the synthesis of block copolymers.

The strategy has been successfully implemented to prepare well-defined poly(methylene-*b*-styrene) (PM-*b*-PS) **29** (Scheme 13).[30] Two living polymerizations were utilized to control the molecular weight of each block. The polystyrene block **26** was installed from initiator **25** via nitroxide mediated polymerization of styrene. The hydroxyl group of polystyrene block **26** was then allylated and hydroborated to give organoborane macroinitiator **28**. Polyhomologation with ylide **1** introduced the polymethylene block of copolymer **29**. Control of molecular weight of both PS and PM blocks was confirmed by MALDI-TOF and GPC analysis.

The PM-*b*-PS copolymer **29** was evaluated as compatibilizer for blends of PS and PE.[11] PE is immiscible with PS. Two blends PS/PE (50/50) and PS/PM-*b*-PS/PE (50/8/50) were prepared by solution mixing followed by precipitation with hexane. The phase separation was observed by polarized optical microscopy (Figure 7). Two distinct phases, the crystalline PE phase (light area) and the amorphous PS phase (dark area), are visible in the PS/PE (50/50) blend. For the ternary blends PS/PM-*b*-PS/PE (50/8/50) with PM-*b*-PS as the compatibilizer, the size of both PE and PS domains decreases dramatically, approaching a nanocomposite. The PM-*b*-PS copolymer acts as a surfactant to lower the interfacial tension and improve the miscibility between the two phases.

Copolymers containing very disparate blocks have also been prepared. Poly(ethylene glycol-*b*-methylene) (PEG-*b*-PM) was prepared by polyhomologation from commercially available methoxy terminated poly(ethylene glycol) (mPEG) **30**

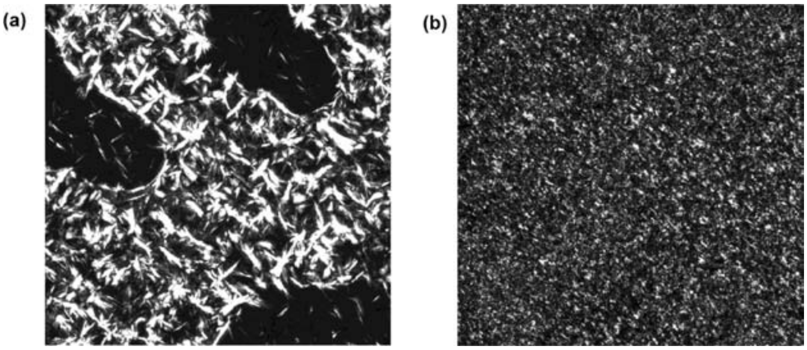
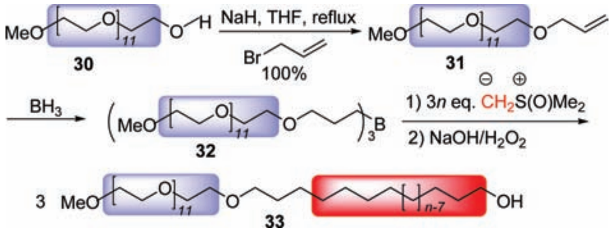


FIGURE 7. Polarized optical micrographs of polymer blends. (a) Two homopolymers with PE/PS = 50/50. (b) Two homopolymers and PM-*b*-PS copolymer with PS/PS-*b*-PM/PE = 50/8/50.

SCHEME 14. Procedure for the Synthesis of Poly(ethylene glycol-*b*-methylene) **33**

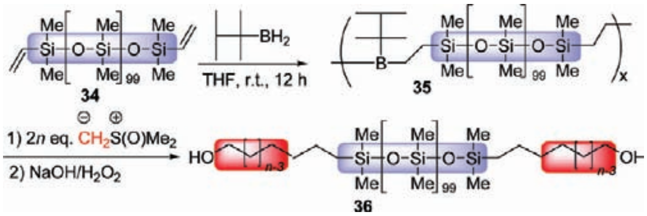


(Scheme 14).[31] The terminal hydroxyl groups of mPEG **30** were allylated and then hydroborated to give macroinitiator **32** which installed the polymethylene block by polyhomologation.

The PEG-*b*-PM copolymer **33** was evaluated as compatibilizer for PE/clay nanocomposites.[32] Delamination of clay to disperse inorganic nanosheets in PE is an important strategy to suppress polymer flammability. Our approach was to use PEG-*b*-PM to intercalate into the galleries of layered silicate via the PEG segment, weakening the interaction between silicate layers and enhancing the organophilicity of the clay surface via the PM segment. Several blends of montmorillonite clay and PEG-*b*-PM copolymer with different PM block lengths were prepared by melt blending, as well as the control samples PEG/clay and PM/clay. Successful intercalation is indicated by an increase in the distance between the silicate layers (*d*-spacing) of the clay from X-ray diffraction analysis. PM oligomers (PM_{105}) do not intercalate into the layered silicate, PM_{105}/clay (12.9 Å) versus pure clay (11.8 Å). On the other hand, PEG_{12}-*b*-PM_{101} and PEG_{12}-*b*-PM_{51} intercalate into the galleries of layered silicate as effectively as PEG_{12} homooligomer, a known clay intercalater. They increase the *d*-spacings of montmorillonite clay from 11.8 to 17.7, 17.6, and 17.9 Å respectively. We have established a maximium PM block size that a PEG_{12} block can draw into the layered silicate, since PEG_{12}-*b*-PM_{249} does not intercalate (*d*-spacing = 12.3 Å). Final dispersal of the clay into nanosheets may be achieved by melt blending of the modified clay mixture into PE.

The synthesis of ABA triblock polymethylene copolymers requires a modified strategy. α,ω-Divinylpoly(dimethylsiloxane) **34** (PDMS, $\overline{DP} = 100$) was hydroborated with thexyl borane to produce soluble macroinitiator **35**. Thexyl borane can prevent the formation of an insoluble gel for the hydroboration of diolefins. The macroinitiator **35** was then polymerized and oxidized to form triblock copolymer **36** (Scheme 15).[31] GPC analysis of the triblock copolymer **36** shows a unimodal distribution, indicating the siloxane block retained its integrity throughout the polyhomologation and oxidation.

SCHEME 15. Procedure for the Synthesis of ABA Triblock Copolymer Poly(dimethylsiloxane-*b*-methylene) **36**



Aggregates of the PM-PDMS-PM triblock copolymers can be prepared in toluene by cooling from 105 °C to room temperature.[33] Nanodiscs and micrometer-sized crystal plates of the triblock copolymers were observed by atomic force microscopy (AFM) and transmission electron microscopy (TEM), respectively (Figure 8a,b). The formation of PM-PDMS-PM triblock copolymer aggregates is a kinetic rather than thermodynamic process. Nanodiscs are formed upon rapid quenching, since PM segments of the triblock copolymer aggregate immediately to form microcrystallites. However, polymethylene chains may be reorganized to form the larger crystal plates by slow evaporation from dilute solution.

Based on AFM observations, and the fact that PDMS is soluble and PM crystallizes from toluene at room temperature, it was proposed that the core of the nanoaggregate is the insoluble PM block and the PDMS serves as its shell (Figure 8c).[33] Since PM crystallizes and favors parallel chain packing, it was suggested that these nanodiscs have well-ordered chain pack-

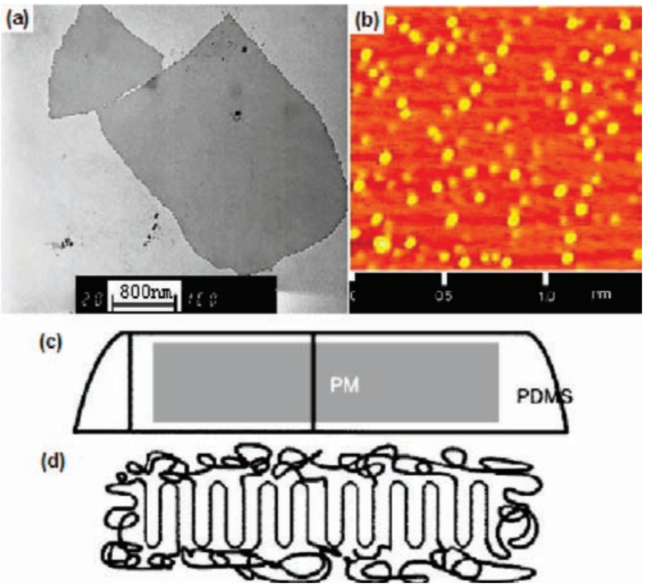


FIGURE 8. (a) TEM image of PM-PDMS-PM crystal plates. (b) Topographic AFM image of PM-PDMS-PM nanoaggregates aspirated on mica from toluene. (c) Schematic illustration of domain structures in PM-PDMS-PM nanodiscs deposited on mica surfaces. (d) Possible chain packing in PM-PDMS-PM nanodiscs.

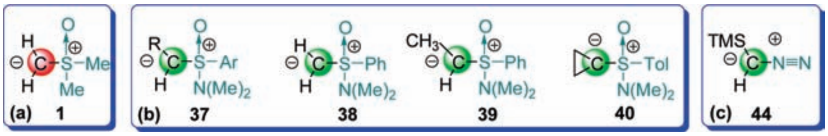
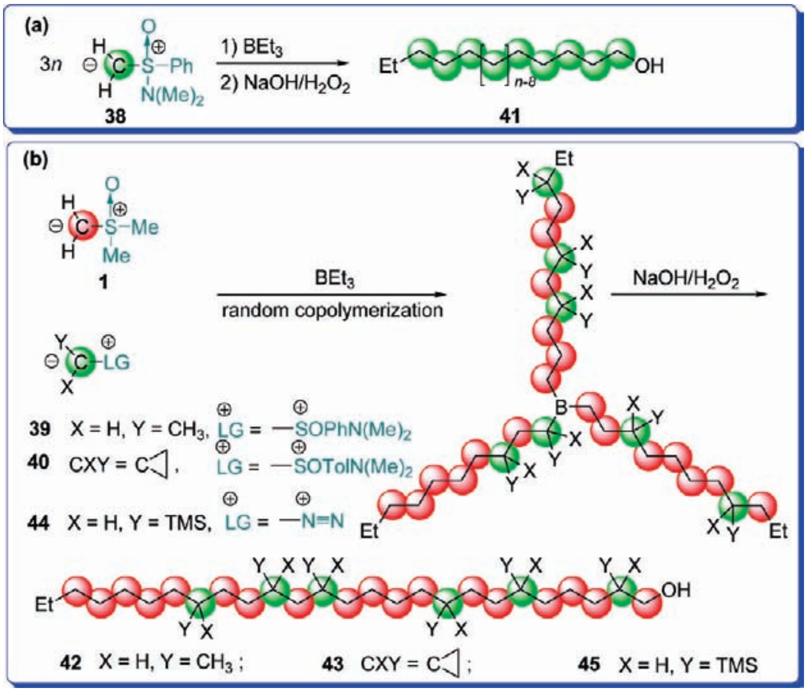


FIGURE 9. Different ylide families as monomers in the polyhomologation reaction. (a) Dimethylsulfoxonium methylide **1**. (b) (Dimethylamino)aryloxosulfonium alkylide **37** and its derivatives: (dimethylamino)phenyloxosulfonium methylide **38**, (dimethylamino)phenyloxosulfonium ethylide **39**, and (dimethylamino)-*p*-tolyloxosulfonium cyclopropylide **40**. (c) Trimethylsilyl diazomethane **44**.

SCHEME 16[a]



[a] (a) Homopolymerization of (dimethylamino)phenyloxosulfonium methylide **38** to produce unsubstituted α-hydroxypolymethylene **41**. (b) Random copolymerization of (dimethylamino)phenyloxosulfonium ethylide **39**, (dimethylamino)-*p*-tolyloxosulfonium cyclopropylide **40**, or trimethylsilyl diazomethane **44** with dimethylsulfoxomium methylide **1** to produce substituted α-hydroxypolymethylene **42**, **43**, or **45**, respectively.

ing inside the PM core which is covered with amorphous PDMS loops (Figure 8d).

The polyhomologation reaction has been combined with ATRP to prepare well-defined polymethylene copolymers, including PM-*b*-PS, polymethylene-*b*-poly(methyl methacrylate) (PM-*b*-PMMA) and polymethylene-*b*-poly(*n*-butyl acrylate) (PM-*b*-P*n*-BuA).[34] These materials have been used to prepare highly ordered microporous films, micelles, and compatilizers for polymer blends.

7. Substituted Polymethylene Derivatives

The introduction of substitutes on a simple carbon backbone such as polyethylene results in a remarkable range of polymer properties.[2,3] A similar range of properties would be available for the polyhomologation reaction by incorporating *substituted* ylides in the monomer mix.

Extension of polyhomologation to the synthesis of substituted carbon backbone polymers requires the availability of substituted ylides that must satisfy several criteria: (1) The ylides must be readily available. (2) They must be stable under the polyhomologation reaction conditions. (3) They must have reasonable reactivity during the polyhomologation reaction. (4) The byproduct from the polymerization should not inhibit the polyhomologation reaction. The (dimethylamino)aryloxosulfonium ylides **37** were found to be suitable candidates (Figure 9b).

The *unsubstituted* ylide **38** is homopolymerized to produce polymethylene **41** with controlled MW and low PDI (Scheme 16a).[35] This established the (dimethylamino)aryloxosulfonium ylide family **37** to be a suitable monomer for the polyhomologation reaction.

However, efforts to homopolymerize **39** or **40** with a borane initiator/catalyst were unsucessful.[35,36] This observation can be understood in terms of the intermediate in the reaction. The introduction of a secondary/tertiary carbon at boron increases steric crowding at the boron center and

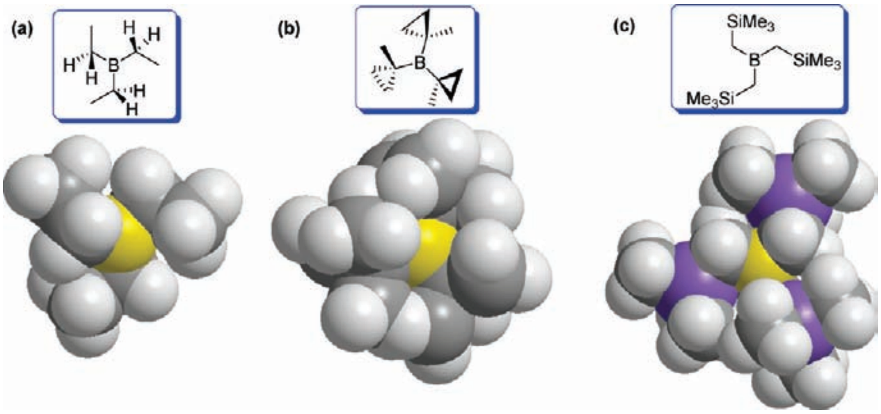


FIGURE 10. Space filling models of (a) triethylborane, (b) tris(1-methylcyclopropyl)borane, and (c) tris(trimethylsilylmethyl)borane, the putative catalytic centers for the homopolymerization of **38**, **40**, and **44**.

decreases reactivity toward addition of the next substituted ylide. This is supported by the comparison of molecular models between triethylborane and tris(1-methylcyclopropyl)borane (Figure 10a,b).[36] The short C−B bond distance compounds the steric demands of the three cyclopropyl groups on the borane and renders the boron atom inaccessible to attack by the tertiary ylide **40**, preventing subsequent addition of ylide **40** and its homopolymerization.

Tri-*sec*-butylborane does however react with an excess of *unsubstituted* methylide **1**, which suggests that following addition of a substituted ylide, there will be a strong tendency to add a methylene group from an unsubstituted ylide.[35] The newly added methylene groups can moderate the steric crowding at the boron center and make it accessible to attack by the substituted ylide. The copolymerization between secondary/tertiary ylide **39** or **40** and primary ylide **1** offers the potential to prepare *substituted* carbon backbone polymers.

In one example, (dimethylamino)phenyloxosulfonium ethylide **39** was copolymerized with ylide **1** to form a *substituted* carbon chain (Scheme 16b, X = H, Y = CH_3).[35] The resultant polymer, hydroxyl-terminated poly(ethylidene-*co*-methylidene) **42**, has the same chemical composition as an ethylene-propylene copolymer. However, in this case, the carbon backbone is constructed *one carbon at a time* from CH_2 and $CHCH_3$ fragments. Both NMR spectra and SEC analyses of the polymer indicate that the molecular weight of the polymer is controlled with low PDI values.

The ratio of methylidene (CH_2) to ethylidene ($CHCH_3$) groups in the polymer was established by quantitative ^{13}C NMR analysis, and it is very close to that calculated from the reaction feed ratio. This indicates excellent control of polymer composition.[35]

The polyhomologation reaction has also been used with tertiary ylide **40** (Scheme 16b, CXY = cyclopropyl).[36] (Dimethylamino)-*p*-tolyloxosulfonium cyclopropylide **40** can be copolymerized with ylide **1**, resulting in the cyclopropyl-containing polymer **43** with tailored end groups and MW.

Early reports of C1 polymerization utilized diazo compounds as a monomer source.[7] More recent work using transition-metal catalysts has achieved high molecular weight C1 polymers, in some cases with stereochemical control.[37−39] The chemical similarities between diazo compounds and ylides permit their utilization in the polyhomologation reaction for the controlled synthesis of *substituted* carbon backbone polymers. For example, trimethylsilyl diazomethane (TMD) **44**, a source of the trimethylsilylmethylidene group ($CHSiMe_3$), was used as a comonomer in the polyhomologation reaction (Figure 9c).

TMD **44** failed to homopolymerize with $BH_3 \cdot SMe_2$.[19] The reaction stops at tris(trimethylsilylmethyl)borane. A space filling model of tris(trimethylsilylmethyl)borane (Figure 10c) reveals the sterically hindered boron center is no longer accessible to the bulky monomer **44**.

However, TMS-substituted copolymethylene **45** can be prepared by the copolymerization of TMD **44** with ylide **1** (Scheme 16b, X = H, Y = TMS).[19] The experimental molecular weight of **45** was found to be higher than the calculated value, and the PDI is relatively high by polyhomologation standards. We have proposed this is due to the steric hindrance from the bulky TMS methylene group and lowered Lewis acidity of boron center by the overlap of the empty p-obital of boron with the C−Si σ bond. These organoborane complexes react more slowly with the monomer, which retards the reaction rate and spreads out the molecular weight distribution.

The development of new monomers expands the variety of polymer material available from boron-mediated polymerization. Mioskowski et al. developed allylic arsonium ylides for the synthesis of poly(propenylene/propenylidene).[40] In this case, the boron-mediated polymerization involves a [1,3] sigmatropic rearrangement of the allylic boron intermediate. Based on the double bond substitution of the allylic arsonium ylides, either C1 or C3 polymerization can take place.

8. Conclusion and Outlook

A new approach for the controlled synthesis of polymethylene has been developed. A Lewis acidic organoborane functions as initiator/catalyst, and dimethylsulfoxonium methylide **1** serves as monomer to produce perfectly linear polymethylene. Association of ylide **1** and trialkylborane forms a zwitterionic complex, which subsequently undergoes a rate-limiting 1,2-migration step to insert a methylene unit into a boron-terminated polymer chain. The polymer backbone is built up one carbon at a time. The polyhomologation reaction is a living polymerization, providing accurate control over molecular weight with low polydispersity. Telechelic polymethylene is produced from a functionalized borane initiator/catalyst and a post-polymerization transformation of a boron−carbon bond. Cyclic and polycyclic organoborane initiators coupled with post-polymerization modification permit construction of novel polymenthylene topologies including three-arm star polymers, giant tubelike structures, and macrocycles. The polyhomologation can be combined with other living polymerizations to synthesize AB and ABA polymethylene block copolymers that can self-assemble into complex architectures ranging from micrometer-sized crystal plates to nanodiscs or function as polymer blending agents. Expansion of the pool of monomers to diazo compounds and (dimethylamino)aryloxosulfonium alkylides provide access to substituted carbon backbone polymers.

Full utilization of C1 polymerization has not yet been realized. This chemistry offers opportunities for synthesizing polymers and topology not readily available by traditional olefin polymerization. Remaining challenges that engage our research efforts include catalyst development for synthesis of fully substituted carbon backbone polymers, controlled synthesis of defined architectures that include block, comb, and network polymers, and development of more environmentally friendly polymerization conditions.

We thank the Chemistry Division of the National Science Foundation for financial support of this work. We also wish to thank the Dow Chemical Co. and ExxonMobil Research & Engineering Co. for assistance with the analysis of high molecular weight polymethylene, and Leah Brigit Cleary for helpful discussions.

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Jun Luo received her B.S. degree in polymer science and engineering from the University of Science & Technology of China (2006). As an undergraduate student, she worked in the laboratory of Prof. Ruke Bai. She is currently a Ph. D. student in Prof. Kenneth J. Shea's group at the University of California, Irvine. Her research focuses on the synthesis of novel architectures of high molecular weight polymethylene.

Kenneth J. Shea was born in Queens, New York. He received his B.S. degree from the University of Toledo and Ph.D. degree from the Pennsylvania State University (1973). Following postdoctoral studies at Cal Tech, he joined the faculty at the University of California, Irvine where he is currently Professor of Chemistry and Chemical Engineering & Material Science. His research interests are in synthetic and mechanistic organic chemistry, the development of new polymerization reactions, synthetic antibodies, and the molecular design of hybrid materials.

FOOTNOTES

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