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Synthesis of Polymethylene Block Copolymers by the Polyhomologation of Organoboranes

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We recently reported a living polymerization for the synthesis of polymethylene.[1] Ylides, such as dimethylsulfoxonium methylide (**1**), serve as monomers. Alkyl boranes function as the initiator/catalyst. The methylene chain is built up one carbon at a time by repetitive homologation at all three alkyl substituents on boron, giving rise to a star polymethylene organoborane, **2** (Scheme 1).

Polyhomologation is a living polymerization. The molecular weight of polymethylene is controlled by the molar ratio of ylide **1** to alkyl borane. Polydispersities (PDI's) as low as 1.01 have been obtained. The primary polyhomologation product, star organoborane **2**, may be used to functionalize the terminus of the polymer chain, i.e., **3**, as well as synthesize novel polymethylene architectures.[2] Finally, since functional organoboranes may be employed as initiator/catalyst; polyhomologation can introduce functionality at both ends of the polymethylene chain.[3] Conventional ethylene polymerization, while extraordinarily efficient, does not provide for such control of molecular weight or functionality.[4]

In this communication we report a significant development in polyhomologation chemistry, the synthesis of polymethylene block copolymers. Examples include synthesis of amphiphilic block copolymers, as well copolymers containing hard and soft segments. The incompatibility of the polymer blocks allows for “tunable” phase separation, as well as designed nanoarchitectures. These copolymers have potential applications as dispersants, detergents, flocculants, and blending agents.[5,6] AB and ABA block copolymers of poly(ethylene glycol-*b*-methylene) and poly(dimethylsiloxane-*b*-methylene) were chosen as the initial targets of this research. While poly(ethylene glycol-*b*-ethylene) copolymers are known, the synthesis of controlled molecular weight blocks has been difficult to acheive.[6,7] To our knowledge, this is the first synthesis of poly(dimethylsiloxane-*b*-methylene).

Table 1. Synthesis of mPEG-PM Copolymers Using Borane Initiator 6

entry	theoretical $\overline{DP}^a$	^{1}H NMR $\overline{DP}^{b,c}$	polymerization temp (°C)	% yield
1	50	62	60	83
2	75	101	60	91
3	150	187	60	86

[a] Theoretical $\overline{DP}$ = (mol of ylide)/(mol of borane **6**) × 3. [b] ^{1}H NMR $\overline{DP}$ = (sum of methylene areas at 1.5 and 1.3−1.1 ppm)/(methoxy area at 3.5 ppm) × $^3/_2$. [c] ^{1}H NMR carried out at 90 °C in toluene-d_8.

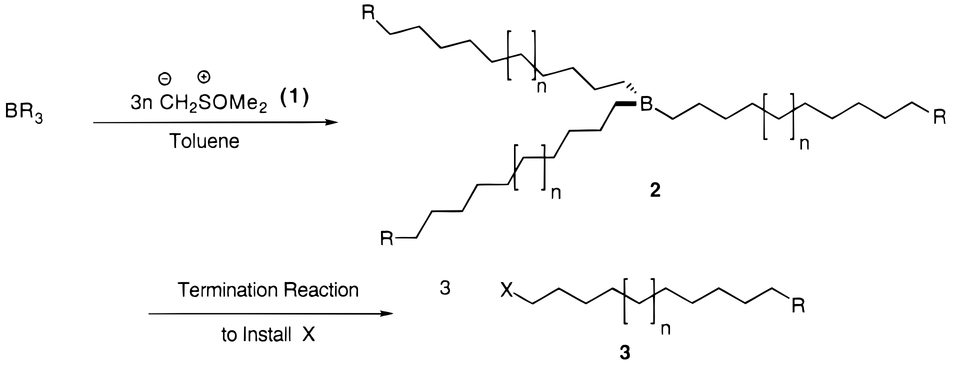
Poly(ethylene glycol-*b*-methylene) was prepared from commercially available methoxy terminated poly(ethylene glycol) (mPEG) as shown in Scheme 2. The mPEG **4** was quantitatively allylated by reaction with NaH and allyl bromide in refluxing THF. Hydroboration was carried out by reacting 3.01 equiv of allylated mPEG **5** with borane at 0 °C in THF.[8]

The polyhomologation was carried out by rapidly adding a THF solution of **6** to a preheated solution (60 °C) of ylide **1** in toluene (Scheme 2). After ylide consumption (ca. 20 min at 60 °C), aqueous solutions of NaOH and H_2O_2 were added to the reaction mixture followed by stirring for 3 h at 25 °C. After concentration to approximately half the initial volume, the block copolymer **7** was precipitated by addition of hexanes. The overall yield of poly(ethylene glycol-*b*-methylene) **7** was typically 80%.

Characterization by NMR required developing conditions to obtain homogeneous solutions of copolymer **7**. It was found that mPEG-PM **7** was soluble in toluene-d_8 at 90 °C. The results of these NMR investigations are summarized in Table 1. The theoretical $\overline{DP}$, based on quantitative formation of borane **6**, was lower than the experimental $\overline{DP}$ calculated from ^{1}H NMR using end group analysis. Since borane **6** was prepared in situ, the true concentration is not known exactly;[9] however, changing the mole ratio of ylide to borane **6** gave the anticipated proportional increase in $\overline{DP}$ between sample runs, a finding that is consistent with the living nature of the polyhomologation reaction.

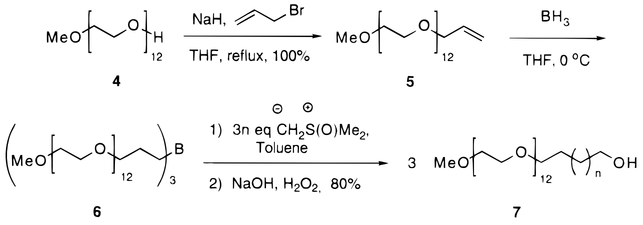
The synthesis of ABA triblock copolymers required a modified strategy. Hydroboration of long chain diolefins with borane can lead to gel formation.[10] For example, when α,ω-divinylpoly (dimethylsiloxane) **8** was hydroborated with borane, an insoluble gel was produced which was not suitable for use as a polyhomologation initiator.

Scheme 1



10.1021/ma981934z CCC: $18.00

Scheme 2



Scheme 3

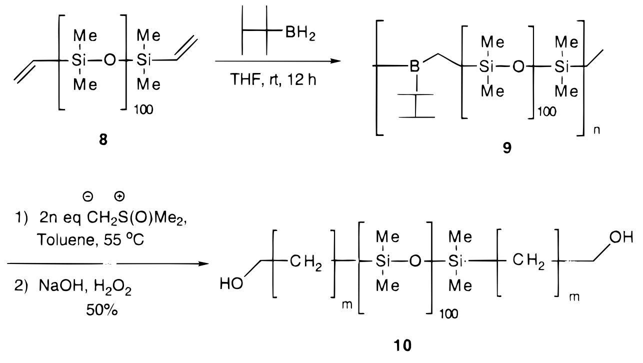


Table 2. Synthesis of PM−PDMS−PM Block Copolymers (10) Using Borane Initiator 9

entry	theoretical $\overline{DP}$[a]	^{1}H NMR $\overline{DP}$[b,c]	polymerization temp (°C)	% yield
1	55	58	55	91
2	109	105	55	95
3	219	208	55	95

[a] Theoretical $\overline{DP}$ = (mol of ylide)/(mol of borane **9**). [b] ^{1}H NMR carried out in toluene-d_8 at 85 °C. [c] ^{1}H NMR $\overline{DP}$ determined by the ratio (PDMS area at 0.08−0.00 ppm)/(PM area at 1.30−1.10 ppm).

Network formation can be suppressed by reducing the number of active BH groups in the hydroborating agent. We have previously found that the thexyl group does not undergo migration during polyhomologation,[11] thus, hydroboration of diolefins with thexyl borane, produces viscous solutions (but no gels).

α,ω-Divinylpoly(dimethylsiloxane) **8** (PDMS, $\overline{DP}$ = 100) was hydroborated with thexylborane to generate soluble borane **9**. This was quickly added to excess ylide **1** in toluene. After ylide consumption (ca. 10 min at 55 °C), the polyhomologated borane was oxidized at 0 °C with aqueous solutions of NaOH and H_2O_2. The polymer was precipitated with MeCN, filtered, and washed with toluene. The triblock copolymer **10** was isolated in >90% yield (Scheme 3).

Several triblock copolymers with different polymethylene lengths were synthesized. The results are summarized in Table 2. GPC analysis of triblock **10** showed a unimodal distribution of the ABA triblock indicating the siloxane block retained its integrity through both polyhomologation and basic peroxide oxidation. The data in Table 2 show that the length of the polymethylene chain could be controlled by adjusting the ratio of ylide **1** to organoborane. The spectroscopic behavior of PM−PDMS−PM triblock copolymers indicates solvent-dependent microphase separation. For example, ^{1}H NMR at room temperature in $CDCl_3$ and toluene-d_8 showed *only* the siloxane methyl resonance at 0.07 ppm. The characteristic polymethylene resonance at 1.25 ppm was absent. Only upon heating to 85 °C in toluene-d_8 was the polymethylene resonance observed. These results suggest that in both solvents at room temperature the polymethylene segments are aggregated (microcrystalline) and are not free to undergo rapid rotation to permit relaxation.

In this communication we have demonstrated the utility of the polyhomologation reaction for synthesis of polymethylene(ethylene) block copolymers. A series of AB amphiphilic block copolymers of poly(ethylene glycol)/polymethylene were prepared by the hydroboration-polyhomologation protocol. Control over the chain length of the polymethylene block was achieved by adjusting the initial molar ratio of ylide to organoborane. ABA block copolymers of PM−PDMS−PM were synthesized by a similar approach using thexyl borane as the difunctional hydroborating agent. Polyhomologation is a general method for synthesis of polymethylene copolymers. A report of the scope of this method and the phase behavior of these novel materials will be reported on soon.

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Supporting Information Available: Text given characterization and experimental procedure for all copolymers and figures showing NMR and MS spectra. This material is available free of charge via the Internet at http://pubs.acs.org.

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(8) The hydroboration of allyl mPEG **5** was not regioselective. Oxidation of borane **6** to the corresponding alcohol indicated a 75:25 mixture favoring boron on the terminal carbon.
(9) Oxidation of borane **6** to the corresponding alcohol did show unreacted allyl mPEG **5** (ca. 23%). This may be the result of incomplete hydroboration or an understated borane (BH_3·THF) concentration.
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