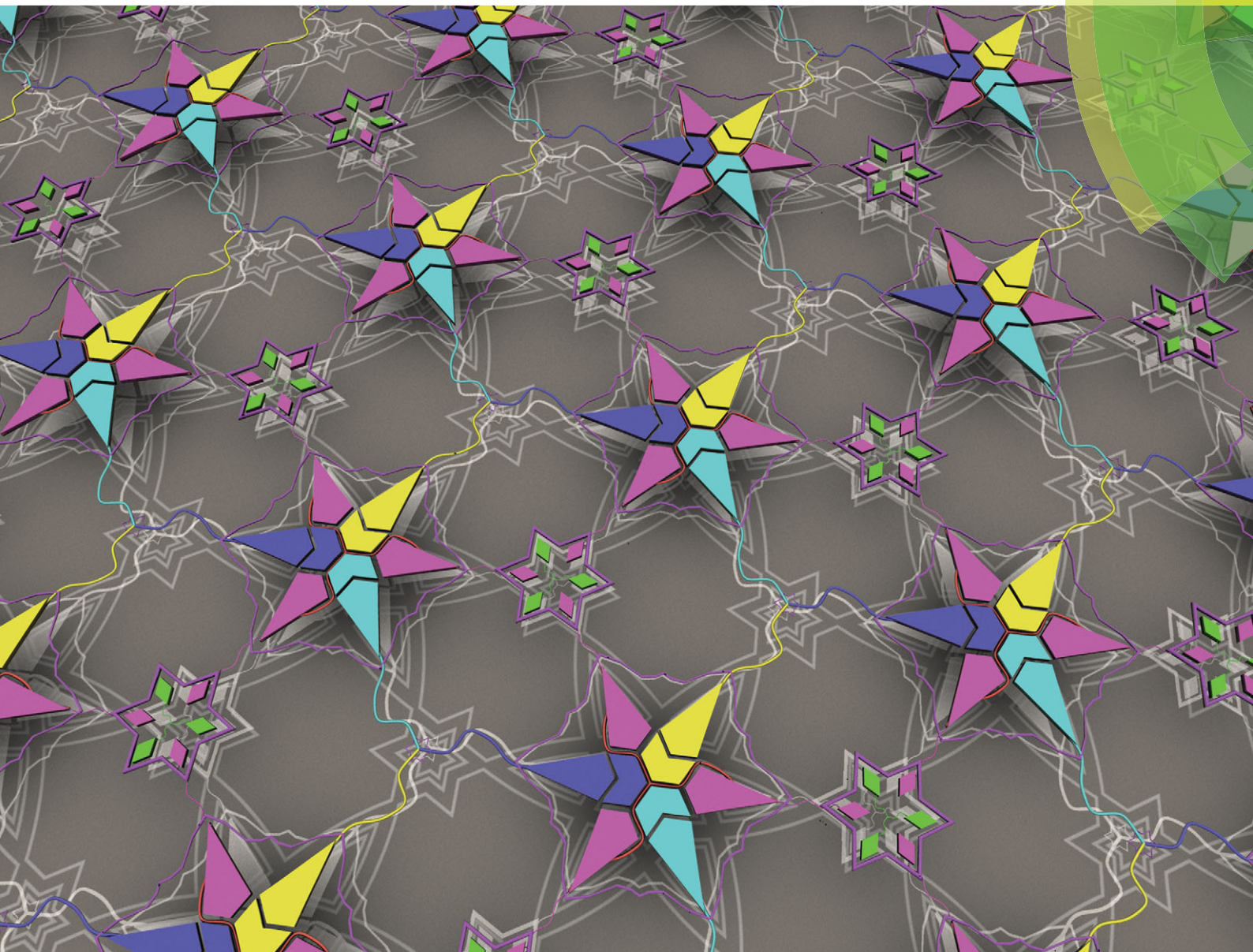


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# Polyhomologation based on *in situ* generated boron-thexyl-silaboracyclic initiating sites: a novel strategy towards the synthesis of polyethylene-based complex architectures†

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**A novel strategy, based on the *in situ* generated boron-thexyl-silaboracyclic initiating sites for the polyhomologation of dimethylsulfoxonium methylide, has been developed for the synthesis of complex polyethylene-based architectures. As examples, the synthesis of a 4-arm polyethylene star, three (polystyrene)(polyethylene)<sub>2</sub> 3-miktoarm stars and a PE-branched double graft copolymer is given.**

Polyethylene (PE), the largest volume commodity polymer in the world, is indispensable in many applications ranging from packaging to precision-processed materials.<sup>1</sup> The low cost, excellent physical properties, easy processability and recyclability of PE have led to its commercial success.<sup>2</sup> However, the poor compatibility of PE with other polymers limits its further applications. To overcome this deficiency, the development of PE-based (co)polymeric materials with novel architectures is needed.<sup>3</sup>

Recently, Shea developed a living polymerization procedure leading to linear well-defined hydroxyl-terminated polymethylene (polyethylene).<sup>4</sup> The general mechanism involves the formation of a complex between an ylide (monomer) and an organoborane (initiator) followed by migration/insertion of  $-\text{CH}_2-$  into the initiator. As a consequence, the methylene groups are randomly inserted one by one (C1 polymerization) into the three arms of the initiator leading to a 3-arm polymethylene star. By oxidizing/hydrolysing the resulted star, an OH-terminated polymethylene (polyethylene) is obtained.

There are four methods for the synthesis of PE-based polymers with different architectures *via* polyhomologation: (1) direct use of the terminal  $-\text{OH}$  of PE-OH for ring-opening polymerization (ROP),<sup>5</sup> or post-polymerization modification of the  $-\text{OH}$  appropriate for atom transfer radical (ATRP),<sup>6</sup> or reversible addition-fragmentation chain-transfer polymerization (RAFT)<sup>7</sup> initiating sites; (2) reaction of PE-OH with functionalized monomers to give macromonomers

followed by (co)polymerization to afford graft copolymers or molecular brushes;<sup>8</sup> (3) stitching reactions to freeze the resultant polyhomologation star structure by transforming the sensitive to oxidation/hydrolysis boron-junction to stable carbon;<sup>9</sup> and (4) design of novel borane initiators.<sup>10</sup>

For example, ROP of  $\epsilon$ -caprolactone initiated directly from the PE-OH macroinitiator with stannous octanoate ( $\text{Sn}(\text{Oct})_2$ ) as a catalyst affords polyethylene-*b*-poly( $\epsilon$ -caprolactone). By transforming the terminal  $-\text{OH}$  of the diblock copolymer to the ATRP initiating site polyethylene-*b*-poly( $\epsilon$ -caprolactone)-*b*-poly(acrylic acid) triblock copolymers have been synthesized.<sup>5a</sup> Well-defined PE brushes have been synthesized by ring opening metathesis polymerization (ROMP) of norbornyl PE-macromonomers prepared by reaction of PE-OH with 5-norbornene-2-carboxylic acid.<sup>8</sup> Stitching reactions have been used to synthesize PE-based linear, macrocarbocyclic and 3-arm star structures.<sup>9</sup> Utilizing novel borane initiators is another efficient way to obtain 3-arm star and multi-block copolymers. For example, polyhomologation of ylides with 1-boraadamantane led to a 3-arm PE<sup>10</sup> and hydroboration of an allyl-terminated polystyrene oligomer with  $\text{BH}_3$  gave an organoborane macroinitiator which by polyhomologation led to poly(ethylene-*b*-styrene) (PE-*b*-PS) block copolymers.<sup>11</sup> Our group synthesized 3-arm-polybutadiene, polystyrene and (polystyrene-*b*-polydiene)borane stars by reaction of the corresponding living macroanions with  $\text{BF}_3 \cdot \text{Et}_2\text{O}$ , which served as macroinitiators for the synthesis of OH-terminated di- and triblock co- and terpolymers.<sup>12</sup>

In this communication, we propose a novel general strategy based on the *in situ* formation of B-thexyl-silaboracyclic structure, having two silicon-connected initiating sites and one blocked, for the synthesis of PE-based complex macromolecular architectures.

To check the principle of this strategy, B-thexyl-methylphenyl-silaboracycle **2** (mixture of **2a** and **2b** isomers), a small equivalent molecule, was prepared by hydroboration of methylphenyldivinylsilane **1** with thexylborane<sup>13</sup> and used *in situ* to promote the polyhomologation of dimethylsulfoxonium methylide (Scheme 1). Details of the synthesis and characterization are given in the ESI.† After hydrolysis of the polyhomologation product, only  $\alpha$ ,  $\omega$ -dihydroxy polymethylene was produced as evidenced by the

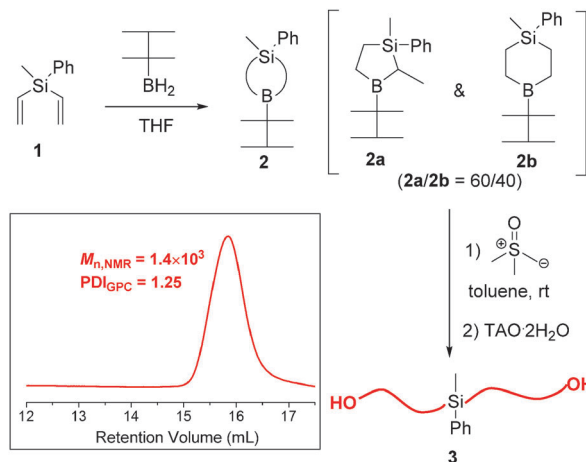
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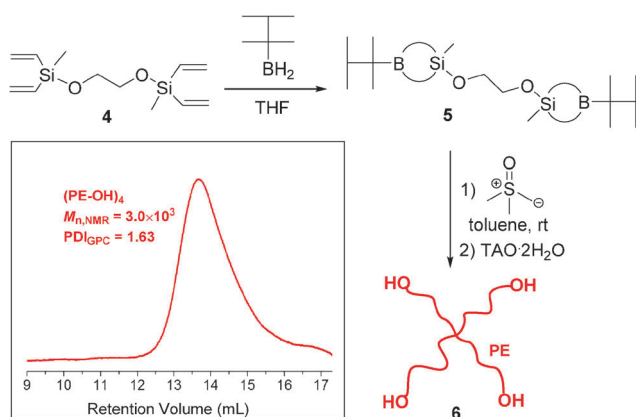
Scheme 1 Synthesis of  $\alpha, \omega$ -dihydroxyl PE and its GPC chromatogram.

appearance of only one peak in the GPC chromatogram and the absence of the hexyl group in the NMR spectrum, meaning that the B-hexyl site is inactive to polyhomologation and all other B-initiating sites (in **2a** and **2b** isomers) are equivalent, in agreement with Shea's work using B-*p*-methoxy-phenylethyl-9-BBN as an initiator.<sup>9</sup> This is easy to explain since after the first insertion of a  $-\text{CH}_2-$  on the boron-tertiary carbon (B-CH) all sites (B- $\text{CH}_2$ ) become equivalent.

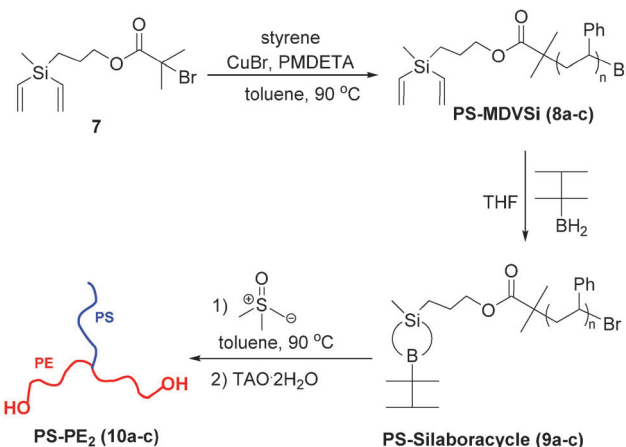
Subsequently, this strategy was employed for the macromolecular design and synthesis of a 4-arm polyethylene star, three (polystyrene)(polyethylene)<sub>2</sub> 3-miktoarm stars and a PE-branched double graft copolymer.

The general reaction scheme for the synthesis of a 4-arm star is given in Scheme 2. The hydroboration of 3,8-dimethyl-3,8-divinyl-4,7-dioxo-3,8-disiladeca-1,9-diene **4** with hexylborane gives bis-B-hexyl-silaboracycles **5**. After treating **5** with excess ylide and subsequent oxidation-hydrolysis reaction using TAO·2H<sub>2</sub>O, 4-arm PE star **6** ( $M_{n,\text{NMR}} = 3.0 \times 10^3$ ,  $\text{PDI}_{\text{GPC}} = 1.63$ ) was obtained (Fig. S2, ESI<sup>†</sup>). Details are given in the ESI.<sup>†</sup>

The synthesis of PE-based 3-miktoarm stars was achieved according to Scheme 3 by combining polyhomologation with ATRP through an heterofunctional initiator, 3-(methyldivinylsilyl)-propyl-2-bromo-2-methylpropanoate **7** (the synthesis procedure is



Scheme 2 Synthesis of 4-arm PE star and its GPC chromatogram.



Scheme 3 Synthesis of PE-based 3-miktoarm star polymers by combination of ATRP and polyhomologation.

given in the ESI,<sup>†</sup> Scheme S4). The 2-bromo-2-methylpropanoate group was used to initiate the ATRP of styrene (CuBr/PMDTA (*N,N,N',N',N',N'*-pentamethyldiethylene-triamine)) and methyldivinylsilyl after transformation to B-hexyl-silaboracycles to initiate polyhomologation. Three samples of divinyl-terminated polystyrene with different molecular weights and low polydispersities have been designed and synthesized (**8a**:  $M_{n,\text{GPC}} = 16.0 \times 10^3$ ,  $\text{PDI}_{\text{GPC}} = 1.22$ ; **8b**:  $M_{n,\text{GPC}} = 11.0 \times 10^3$ ,  $\text{PDI}_{\text{GPC}} = 1.18$ ,  $T_g = 85^\circ\text{C}$ ; **8c**:  $M_{n,\text{GPC}} = 5.2 \times 10^3$ ,  $\text{PDI}_{\text{GPC}} = 1.18$ ) (Fig. 1 and Fig. S3 and S4, ESI<sup>†</sup>). The terminal methyldivinylsilyl group was readily transformed to B-hexyl-silaboracycles by hydroboration with hexylborane resulting in the corresponding macroinitiators for polyhomologation (**9a-c**). High hydroboration efficiencies were indicated by quantitative consumption of the terminal vinyl groups ( $\delta = 5.6$  to 6.2 ppm) revealed by <sup>1</sup>H NMR results. As an example, the NMR spectra of **8a** (before hydroboration) and **9a** (after hydroboration) are shown in Fig. 2 (spectra a and b). The resultant boron-macroinitiators were used *in situ* for the polyhomologation of dimethylsulfoxonium methyllide leading to the corresponding PE-based 3-miktoarm stars.

The success of this strategy was confirmed by both GPC and NMR results (Fig. 1 and 2). After polyhomologation, the peak shifted to a higher molecular weight range keeping the narrow distribution profiles (**10a**:  $M_{w,\text{GPC-LS}} = 506 \times 10^3$ ,  $\text{PDI}_{\text{GPC-LS}} = 1.32$ ; **10b**:  $M_{w,\text{GPC-LS}} = 367 \times 10^3$ ,  $\text{PDI}_{\text{GPC-LS}} = 1.56$ ,  $T_m = 116^\circ\text{C}$ ;

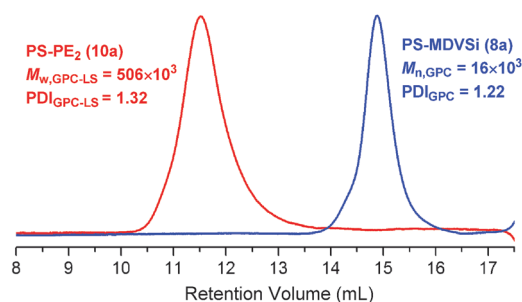


Fig. 1 GPC chromatograms of PS-MDVSis (**8a**) and the corresponding 3-miktoarm star (**10a**).

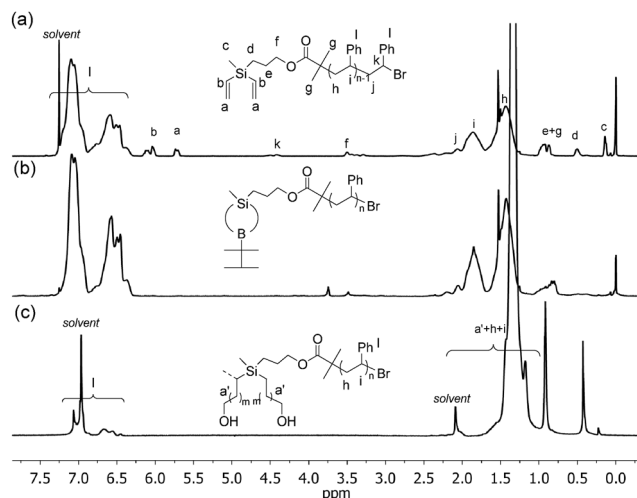
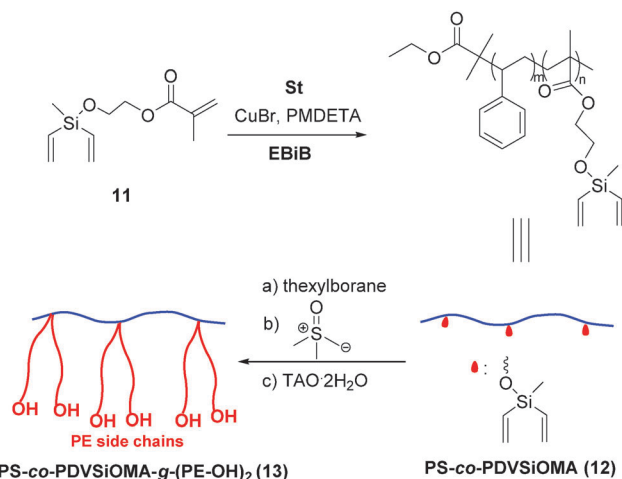


Fig. 2  $^1\text{H}$  NMR spectra of (a) PS-MDVSil (**8a**) (chloroform- $d_2$ , 25  $^\circ\text{C}$ ); (b) PS-Silaboracycle (**9a**) (chloroform- $d_2$ , 25  $^\circ\text{C}$ ); (c) PS-PE<sub>2</sub> (**10a**) (toluene- $d_8$ , 80  $^\circ\text{C}$ ).



Scheme 4 Synthesis of PE-branched double graft copolymer by combination of ATRP and polyhomologation.

**10c:**  $M_{w,\text{GPC-LS}} = 423 \times 10^3$ ,  $\text{PDI}_{\text{GPC-LS}} = 1.35$  (Fig. 1 and Fig. S3 and S4, ESI<sup>†</sup>). Also, the fingerprints of the PS and PE blocks were found in the  $^1\text{H}$  NMR spectrum (Fig. 2c).

A “grafting from” strategy shown in Scheme 4 was developed to synthesize a double graft copolymer. First, copolymerization of styrene with 2-((methyldivinylsilyl)oxy)ethyl methacrylate (DVSilOMA, **11**) (for preparation see ESI<sup>†</sup>, Scheme S6) by ATRP initiated by ethyl 2-bromoisobutyrate (EBIB) with the CuBr/PMDTA catalytic system led to PS-*co*-PDVSilOMA **12**. Then, the pendant divinylsilyl groups were transformed to B-thexylsilaboracycles by hydroboration with thexylborane, followed by polyhomologation. As an example, PS<sub>38</sub>-*co*-PDVSilOMA<sub>3</sub> ( $\text{PDI}_{\text{GPC}} = 1.31$ ) was synthesized (feed ratio 50/4.5).

Hydroboration of PS<sub>38</sub>-*co*-PDVSilOMA<sub>3</sub>/polyhomologation by the resultant macroinitiator leads to PE-branched double graft

copolymer PS-*co*-PDVSilOMA-*g*-(PE-OH)<sub>2</sub> **13** ( $M_{w,\text{GPC-LS}} = 218 \times 10^3$ ,  $\text{PDI}_{\text{GPC-LS}} = 1.35$ ) (see ESI<sup>†</sup>, Fig. S5). High hydroboration efficiency was indicated by the quantitative disappearance of the signal at 5.7–6.2 ppm in  $^1\text{H}$  NMR spectra for vinyl protons. The PS backbone is identifiable in NMR spectra (toluene- $d_8$ , 25  $^\circ\text{C}$ ) and the PE fingerprint is much more evident by increasing the temperature up to 80  $^\circ\text{C}$  (see ESI<sup>†</sup>, Fig. S6).

In conclusion, a novel strategy using the *in situ* synthesized B-thexylsilaboracyclic moieties with two silicon-connected initiating and one blocked sites for polyhomologation was successfully developed. This general strategy opens a new horizon for the synthesis of PE-based complex macromolecular architectures. Only a few examples are given in this communication, *i.e.* a 4-arm polyethylene star, three PS-PE<sub>2</sub> 3-miktoarm stars and a PE-branched double graft copolymer. Combination of this general strategy with other living and living/controlled polymerization techniques will lead to novel architectures such as multi-arm stars (8, 12, 16-arm), H-shaped, molecular brush copolymers, *etc.*

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