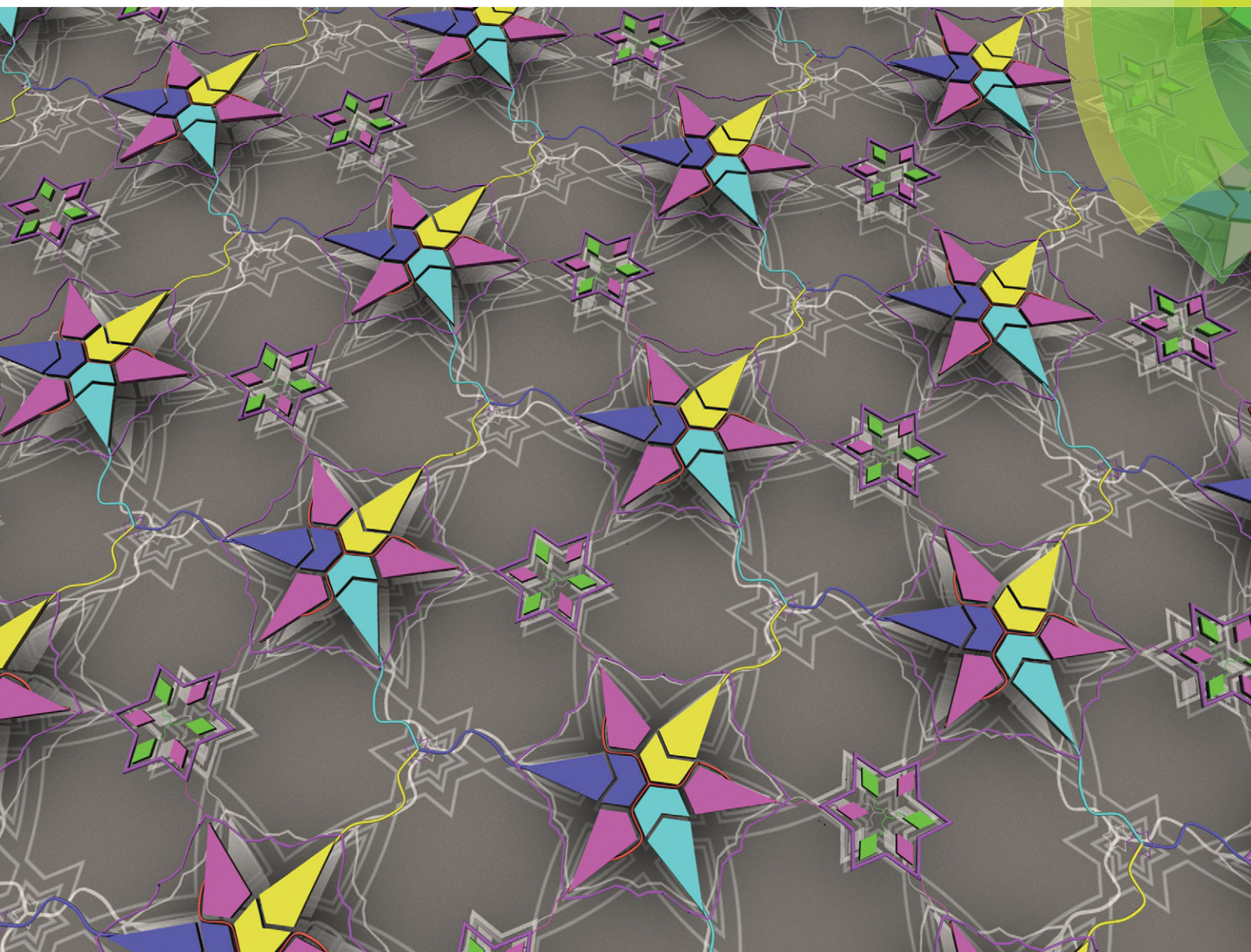


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Polyhomologation based on *in situ* generated boron-thexyl-silaboracyclic initiating sites: a novel strategy towards the synthesis of polyethylene-based complex architectures†

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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)₂ 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.¹ The low cost, excellent physical properties, easy processability and recyclability of PE have led to its commercial success.² 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.³

Recently, Shea developed a living polymerization procedure leading to linear well-defined hydroxyl-terminated polymethylene (polyethylene).⁴ 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),⁵ or post-polymerization modification of the $-\text{OH}$ appropriate for atom transfer radical (ATRP),⁶ or reversible addition-fragmentation chain-transfer polymerization (RAFT)⁷ initiating sites; (2) reaction of PE-OH with functionalized monomers to give macromonomers

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

For example, ROP of ϵ -caprolactone initiated directly from the PE-OH macroinitiator with stannous octanoate ($\text{Sn}(\text{Oct})_2$) as a catalyst affords polyethylene-*b*-poly(ϵ -caprolactone). By transforming the terminal $-\text{OH}$ of the diblock copolymer to the ATRP initiating site polyethylene-*b*-poly(ϵ -caprolactone)-*b*-poly(acrylic acid) triblock copolymers have been synthesized.^{5a} 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.⁸ Stitching reactions have been used to synthesize PE-based linear, macrocarbocyclic and 3-arm star structures.⁹ 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 PE¹⁰ and hydroboration of an allyl-terminated polystyrene oligomer with BH_3 gave an organoborane macroinitiator which by polyhomologation led to poly(ethylene-*b*-styrene) (PE-*b*-PS) block copolymers.¹¹ 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.¹²

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.

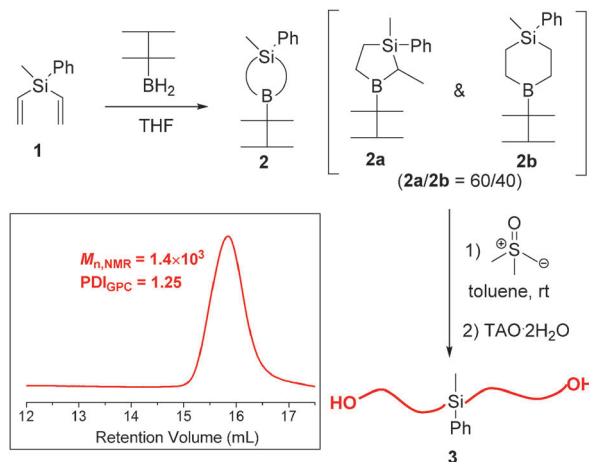
To check the principle of this strategy, B-thexyl-methylphenyl-silaboracycle **2** (mixture of **2a** and **2b** isomers), a small equivalent molecule, was prepared by hydroboration of methylphenyldivinylsilane **1** with thexylborane¹³ and used *in situ* to promote the polyhomologation of dimethylsulfoxonium methylide (Scheme 1). Details of the synthesis and characterization are given in the ESI.† After hydrolysis of the polyhomologation product, only α , ω -dihydroxy polymethylene was produced as evidenced by the

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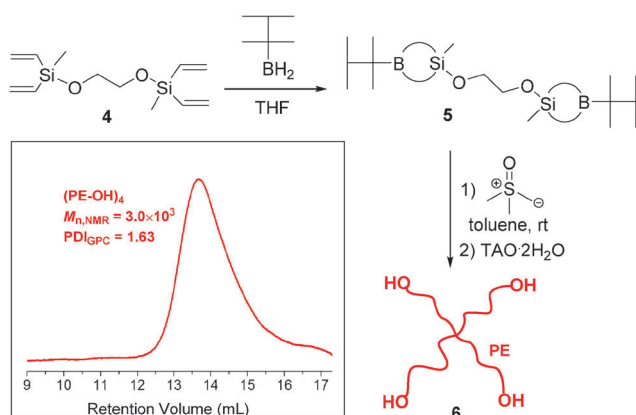
Scheme 1 Synthesis of α, ω -dihydroxyl PE and its GPC chromatogram.

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.⁹ 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- CH_2) become equivalent.

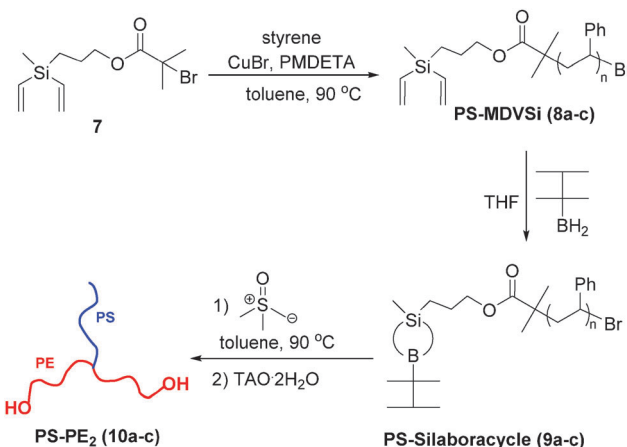
Subsequently, this strategy was employed for the macromolecular design and synthesis of a 4-arm polyethylene star, three (polystyrene)(polyethylene)₂ 3-miktoarm stars and a PE-branched double graft copolymer.

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·2H₂O, 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[†]). Details are given in the ESI.[†]

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,[†] Scheme S4). The 2-bromo-2-methylpropanoate group was used to initiate the ATRP of styrene (CuBr/PMDTA (*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[†]). 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 ¹H 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 methylide 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**: $M_{w,\text{GPC-LS}} = 367 \times 10^3$, $\text{PDI}_{\text{GPC-LS}} = 1.56$, $T_m = 116^\circ\text{C}$;

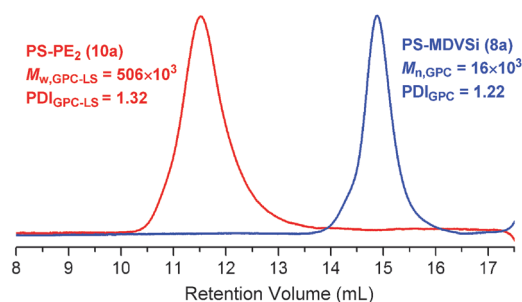


Fig. 1 GPC chromatograms of PS-MDVSil (**8a**) and the corresponding 3-miktoarm star (**10a**).

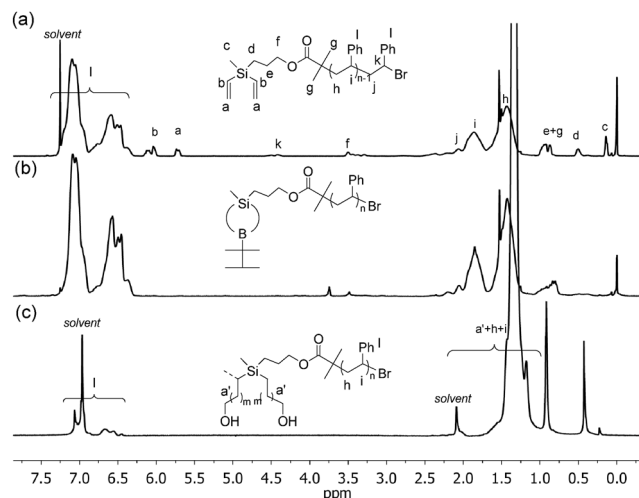
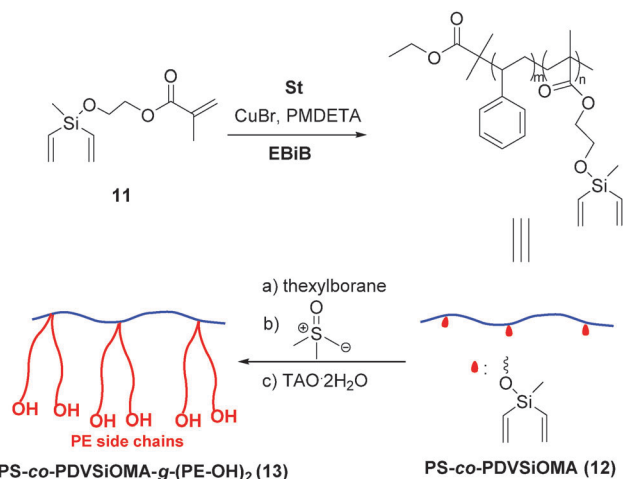


Fig. 2 ^1H NMR spectra of (a) PS-MDVSil (**8a**) (chloroform- d_2 , 25 $^\circ\text{C}$); (b) PS-Silaboracycle (**9a**) (chloroform- d_2 , 25 $^\circ\text{C}$); (c) PS-PE $_2$ (**10a**) (toluene- d_8 , 80 $^\circ\text{C}$).



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 †). Also, the fingerprints of the PS and PE blocks were found in the ^1H 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 † , 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 $_{38}$ -*co*-PDVSilOMA $_3$ ($\text{PDI}_{\text{GPC}} = 1.31$) was synthesized (feed ratio 50/4.5).

Hydroboration of PS $_{38}$ -*co*-PDVSilOMA $_3$ /polyhomologation by the resultant macroinitiator leads to PE-branched double graft

copolymer PS-*co*-PDVSilOMA-*g*-(PE-OH) $_2$ **13** ($M_{w,\text{GPC-LS}} = 218 \times 10^3$, $\text{PDI}_{\text{GPC-LS}} = 1.35$) (see ESI † , Fig. S5). High hydroboration efficiency was indicated by the quantitative disappearance of the signal at 5.7–6.2 ppm in ^1H 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 † , Fig. S6).

In conclusion, a novel strategy using the *in situ* synthesized B-thexyl-silaboracyclic 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 $_2$ 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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