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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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Zhen Zhang,^{a,b} Hefeng Zhang,^{a,b} Yves Gnanou^a and Nikos Hadjichristidis^{*a,b}

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 copolymers are 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 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) following by migration/insertion of -CH₂- 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 -OH of PE-OH for ring-opening polymerization (ROP),⁵ or post-polymerization modification of the -OH to 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

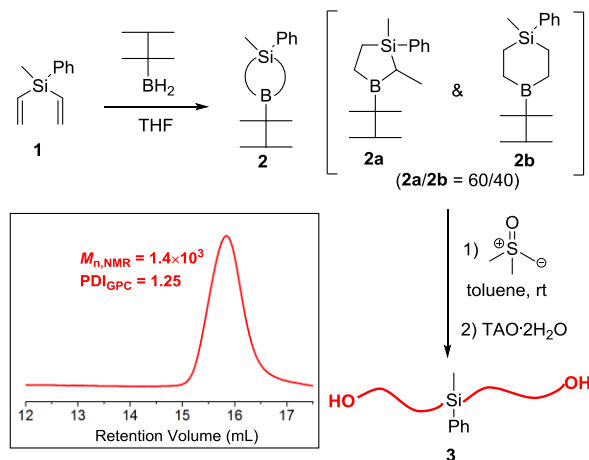
monomers to give a macromonomers followed by (co)polymerization to afford graft copolymers or molecular brushes⁸; 3) stitching reactions to freeze the resulting from polyhomologation star structure by transforming the sensitive to oxidation/hydrolysis boron-junction to stable carbon⁹; and 4) design of novel borane initiators¹⁰.

For example, ROP of ϵ -caprolactone initiated directly from PE-OH macroinitiator with stannous octanoate (Sn(Oct)₂) as catalyst affords polyethylene-*b*-poly(ϵ -caprolactone). By transforming the terminal -OH of the diblock copolymer to 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 multiblock copolymers. For example, polyhomologation of ylides with 1-boraadamantane led to a 3-arm PE¹⁰ and hydroboration of an allyl-terminated polystyrene oligomer with BH₃ 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 BF₃EtO₂, 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, 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-methylphenylsilaborocycle **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 appearance of only one peak in the GPC chromatogram and the absence of the thexyl group in the NMR spectrum, meaning that the B-thexyl 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*-methoxyphenylethyl-9-BBN as initiator.⁹ This is easy to explain since after the first insertion of a $-\text{CH}_2-$ on the boron-tertiarycarbon (B-CH) all sites (B- CH_2) become equivalent.



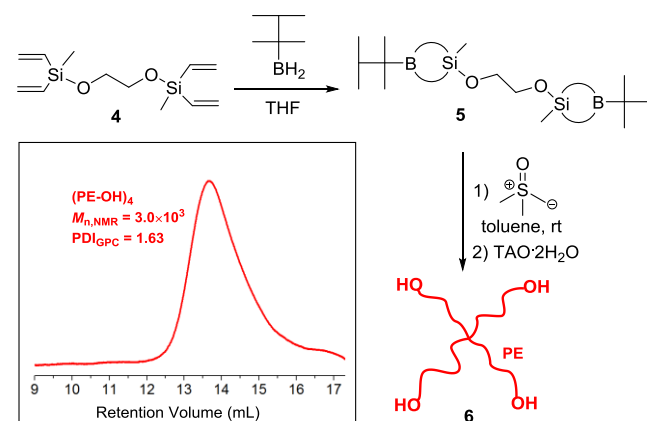
Scheme 1 Synthesis of α , ω -dihydroxyl PE and its GPC chromatogram.

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.

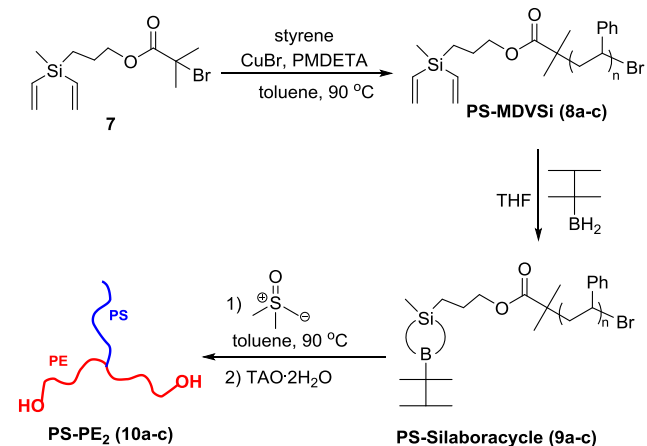
The general reaction scheme for the synthesis of the 4-arm star is given in Scheme 2. The hydroboration of 3,8-dimethyl-3,8-divinyl-4,7-dioxa-3,8-disiladeca-1,9-diene **4** with thexylborane gives bis-B-thexyl-silaboracycles **5**. After treating **5** with excess ylide, followed by oxidation/hydrolysis reaction using TAO·2H₂O, 4-arm PE star **6** ($M_{n,NMR} = 3.0 \times 10^3$, $PDI_{GPC} = 1.63$) was obtained (Figure S2). Details are given in 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 are given in the ESI, Scheme S4). The 2-bromo-2-methylpropanoate group was used to initiate the ATRP of styrene (CuBr / PMDETA (*N,N,N',N',N'*-pentamethyldiethylene-triamine)) and the methyldivinylsilyl after transformation to B-thexyl-silaboracycles to initiate the polyhomologation. Three samples of divinyl-terminated polystyrene with different molecular weights and low polydispersities have been designed and synthesized (**8a**: $M_{n,GPC} = 16.0 \times 10^3$, $PDI_{GPC} = 1.22$; **8b**: $M_{n,GPC} = 11.0 \times 10^3$, $PDI_{GPC} = 1.18$, $T_g = 85^\circ\text{C}$; **8c**: $M_{n,GPC} = 5.2 \times 10^3$, $PDI_{GPC} = 1.18$) (Figure 1, S3 and S4). The terminal methyldivinylsilyl group was readily

transformed to B-thexyl-silaboracycles by hydroboration with thexylborane resulting in the corresponding macroinitiators for polyhomologation (**9a-c**). High hydroboration efficiencies were indicated by quantitatively consumption of the terminal vinyl groups ($\delta = 5.6$ to 6.2 ppm) as revealed by ¹H NMR results. As an example, the NMR spectra of **8a** (before hydroboration) and **9a** (after hydroboration) were shown in Figure 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.



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



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

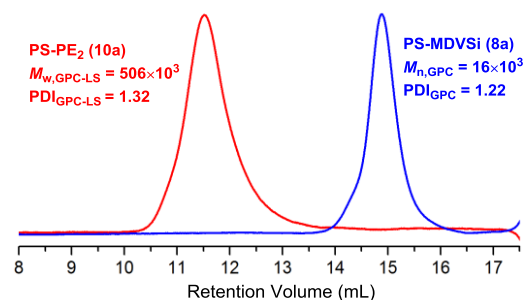


Figure 1 GPC chromatogram of PS-MDVSi (**8a**) and the corresponding 3-miktoarm star (**10a**).

The success of this strategy was confirmed by both GPC and NMR results (Figure 1 and 2). After polyhomologation, the peak moved to higher molecular weight range keeping the narrow distribution profiles (**10a**: $M_{w,GPC-LS} = 506 \times 10^3$, $PDI_{GPC-LS} = 1.32$; **10b**: $M_{w,GPC-LS} = 367 \times 10^3$, $PDI_{GPC-LS} = 1.56$, $T_m = 116$ °C; **10c**: $M_{w,GPC-LS} = 423 \times 10^3$, $PDI_{GPC-LS} = 1.35$) (Figure 1, S3 and S4). Also, the fingerprints of the PS and PE blocks were found in the 1H NMR spectrum (Figure 2c).

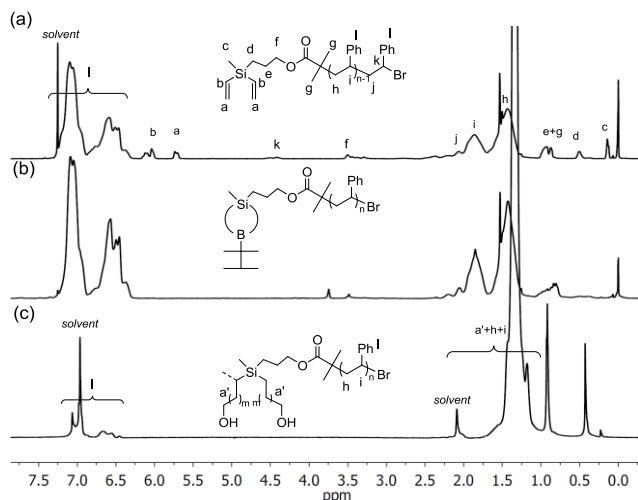
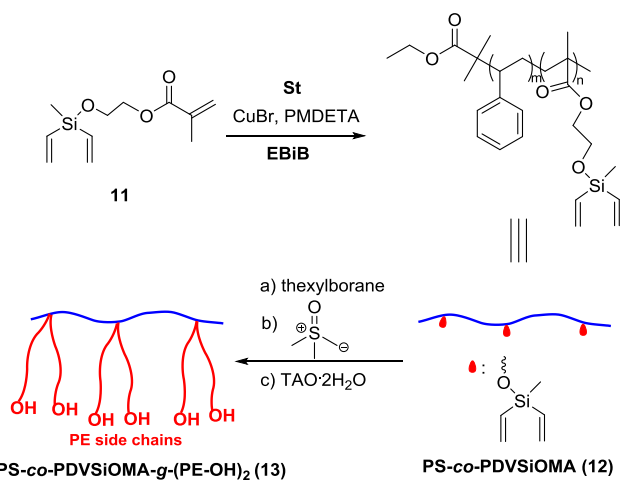


Figure 2 1H NMR spectra of (a) PS-MDVSil (**8a**) (chloroform- d , 25 °C); (b) PS-Silaboracycle (**9a**) (chloroform- d , 25 °C); (c) PS-PE₂ (**10a**) (toluene- d_8 , 80 °C).



Scheme 3 Synthesis of PE-branched double graft copolymer by combination of ATRP and polyhomologation.

A “grafting from” strategy showing in Scheme 3 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-thexyl-silaboracycles by hydroboration with thexylborane, followed by polyhomologation. As an example, the synthesis of PS₃₈-*co*-PDVSilOMA₃ ($PDI_{GPC} = 1.31$) is given (feed ratio 50/4.5).

Hydroboration of PS₃₈-*co*-PDVSilOMA₃/polyhomologation by the resultant macroinitiator lead to PE-branched double graft copolymer PS-*co*-PDVSilOMA-*g*-(PE-OH)₂ **13** ($M_{w,GPC-LS} = 218 \times 10^3$, $PDI_{GPC-LS} = 1.35$) (see ESI, Fig. S5). High hydroboration efficiency was indicated by quantitatively disappearance of the signal at 5.7-6.2 ppm in 1H NMR spectra for vinyl protons. The PS backbone is detectable in NMR spectra (toluene- d_8 , 25 °C) and the PE fingerprint is much more evident by increasing the temperature up to 80 °C (see ESI, Fig. S6).

In conclusion, a novel strategy using the *in situ* synthesized B-thexyl-silaboracyclic moiety with two silicon-connected and one blocked initiating 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. 4-arm polyethylene star, PS-PE₂ 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-shape, molecular brush copolymers, etc.

Notes and references

King Abdullah University of Science and Technology (KAUST), Thuwal 23955, Saudi Arabia.

^a Physical Sciences and Engineering Division, KAUST Catalysis Center, Polymer Synthesis Laboratory.

^b Physical Sciences and Engineering Division.

† Electronic Supplementary Information (ESI) available: Experimental details as well as supporting data including kinetic experiment data, SEC profiles of obtained polypeptides are presented in the supporting information. See DOI: 10.1039/c000000x/

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