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REVIEW

C1 Polymerization: a unique tool towards polyethylene-based complex macromolecular architectures

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The recent developments in organoborane initiated C1 polymerization (chain grows by one atom at a time) of ylides opens unique horizons towards well-defined/perfectly linear polymethylenes (equivalent to polyethylenes, PE) and PE-based complex macromolecular architectures. The general mechanism of C1 polymerization (polyhomologation) involves the formation of a Lewis complex between a methylene (monomer) and a borane (initiator), followed by migration/insertion of a methylene into the initiator and after oxidation/hydrolysis to afford OH-terminated polyethylenes. This review summarizes efforts towards conventional and newly discovered borane-initiators and ylides (monomers), as well as a combination of polyhomologation with other polymerization methods. Initial efforts dealing with C3 polymerization and the synthesis of the first C1/C3 copolymers are also given. Finally, some thoughts for the future of these polymerizations are presented.

1. Introduction

Polyethylene, one of the most valuable synthetic/industrial polymers in the world, has been applied in products ranging from grocery bags to high-performance fibers or medical devices.^{1,2} The versatility of PE-based material stems from its properties including good crystallinity, thermal stability, mechanical strength and so on.³ Developing new topologies will broaden the applications of PE-based materials, since polymer properties, such as elasticity, density and viscoelastic behavior are highly influenced by polymer macromolecular architecture. The traditional ethylene polymerization methods could not fully fulfil the increasing demand of well-controlled polyethylene materials.⁴ Therefore, efforts focusing on the synthesis of well-defined PE and PE-based polymer architectures are still highly demanded.

Until now, only a limited number of methods can achieve well-defined PE-based polymers.⁵ Anionic polymerization of butadiene and sequential hydrogenation of the obtained 1,4-polybutadiene is one of the methods to achieve well-defined PE. However, the produced PE is not 100% linear because of the unavoidable 1,2-units generated during the polymerization.⁶ Hydrogenation of poly(cyclooctadiene) from the ring-opening metathesis polymerization (ROMP) of cyclooctadiene using Grubbs' catalysts can give a linear PE without sidechains but the polydispersity is high.⁷ Living olefin polymerization of ethylene is a promising way to achieve well-defined PEs, however, side chains are unavoidable.⁸

The homopolymerization of diazomethane (CH_2N_2) was the first known synthetic route to polymethylene, PM (equivalent to PE) *via* C1 polymerization,⁹ a totally different way compared to the traditional polymerization of ethylene (C2 polymerization). Later, different diazo compounds including some reasonably stable diazoacetates or diazoketones have been used as C1 monomers with different catalysts to produce poly(substituted methylene) materials.¹⁰ However, the diazo compound explosive nature is not at all practical from a synthetic point of view and limits their use.

Developing a new and convenient controlled/living polymerization method to synthesize well-defined PM (PE) is still needed. In 1997, Shea and co-workers, inspired from the well-known in organic chemistry homologation reaction,¹¹ discovered a borane initiated/mediated C1 living polymerization of dimethylsulfoxonium.¹² This C1 polymerization, coined by Shea polyhomologation, has been proven as an efficient tool to synthesize well-defined and perfectly linear hydroxyl-terminated polyethylene. The general mechanism involves the formation of an organoboron "ate" complex (zwitterionic intermediate) formed by attack of the nucleophilic dimethylsulfoxonium methylene (monomer) on the Lewis acidic borane (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 with boron at the junction point. After oxidizing/hydrolyzing the 3-arm boron star, an OH-terminated polymethylene (polyethylene) is obtained (Scheme 1).¹³ The chemical shift of trialkylboranes to tetraalkylborate complex in the ^{11}B NMR spectra indicates the formation of the organoboron "ate" complex (Figure 1, left).¹⁴ Additional mechanism studies, such as kinetic studies, X-ray diffraction structure of surrogate "ate" complex and computational study (Figure 1, right) have also been applied to better comprehend

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this polyhomologation reaction.^{14,15} This new attractive, efficient and metal-free polymerization reaction has been utilized to synthesize different well-defined PE-based polymers.^{5,13}

Scheme 1. Polyhomologation reaction and proposed mechanism

Figure 1. Upper: ^{11}B NMR spectra in toluene (a) tri-*n*-hexylborane at 40 °C, (b) tri-*n*-hexylborane/ylide complex at -15 °C, (c) trialkylborane, with one more CH_2 at 40 °C. The small peak at 48 ppm corresponds to boronic ester impurities. Down: (a) Single-crystal X-ray analysis of ylide- BF_3 complex, (b) ylide- BMe_3 complex obtained from a DFT/B3LYP/6-311G (d,p) calculation. Copyright 2010, American Chemical Society.¹³

In this review, the development of boron initiators and ylide monomers in polyhomologation, as well as the synthesis of well-defined PE-based homo/copolymers with different macromolecular architectures, by combining polyhomologation with other polymerization methods, will be emphasized. Initial efforts dealing with C3 polymerization and the synthesis of the first C1/C3 copolymers will also be given. Finally, some thoughts for the future of these C1 and C3 polymerizations are discussed.

2. Borane Initiators

2.1 Tri(macro)alkylboranes (Two or three active sites).

By using different functionalized borane initiators, novel well-defined functionalized PEs have been successfully achieved. For example, functionalized trialkylboranes, derived from hydroboration of different alkene compounds (**a-l**) with BH_3 , were used as initiators for the polymerization of dimethylsulfoxonium methylide resulting

in different linear telechelic PEs with hydroxyl, aryl, biotin and fluorescent moieties, among others, end-groups (Scheme 2). The molecular weight of these α,ω -difunctionalized PEs ranges from 650 to 20000 g mol^{-1} and the polydispersity $\bar{D} < 1.1$.^{16,17} Obviously, more functional boranes will lead to more diverse functionalized PEs.

Scheme 2. Synthesis of α,ω -difunctionalized PEs from various functionalized organoborane initiators

Scheme 3. Synthesis of block copolymers by using different macroborane initiators for the polyhomologation of the methylide

Different block copolymers have been successfully synthesized by Shea's group through polymeric borane initiators. A polystyrene (PS) containing organoborane macroinitiator $(\text{PS})_3\text{B}$, derived from nitroxide-mediated polymerization (NMP) of styrene and sequential transformation of $-\text{OH}$ to allyl group, followed by hydroboration with $\text{BH}_3\text{S}(\text{Me})_2$, was used to polymerize dimethylsulfoxonium methylide and afford PS-*b*-PE block copolymers [Scheme 3, (1)].¹⁸ These diblock copolymers are efficient compatibilizers of PE/PS blends, since in their presence the miscibility between PE and PS phases was improved dramatically (Figure 2).¹³ By using the same strategy, mPEG-*b*-PE block copolymers were synthesized by $(\text{mPEG})_3\text{B}$ initiated polyhomologation of the methylide [Scheme 3,

(2)].¹⁹ After hydroboration of the xylborane (the xyl group was employed as blocking group) with α,ω -divinylpoly(dimethylsiloxane) (α,ω -divinyl-PDMS) and polyhomologation, ABA type triblock copolymers PE-*b*-PDMS-*b*-PE were produced [Scheme 3, (3)].¹⁹ The NMR characterization (in both CDCl₃ and toluene-*d*₈) of the triblock copolymers revealed microphase separation at room temperature due to the poor solubility of PE blocks. In toluene, these triblock copolymers form nanoaggregates as observed by AFM and TEM.^{19b}

Figure 2 Polarized optical graphs of PE/PS blends in the absence and presence of PS-*b*-PE: (a) PE/PS = 50/50; (b) PS/PS-*b*-PE/PE = 50/8/50. Reproduced with permission. Copyright 2010, American Chemical Society.¹³

In 2013, our group developed a new one-pot method to synthesize PE-based diblock copolymer by using anionic polymerization in combination with polyhomologation through BF₃Et₂O, serving as a “bridge molecule”. This approach involves the synthesis of 3-arm PBd (polybutadiene) or PS macroborane initiators by reacting the corresponding living macroanions with BF₃Et₂O, and sequential *in situ* polyhomologation of dimethylsulfoxonium methylide to form 3-arm star block copolymers. By oxidation/hydrolysis of the 3-arm star block copolymers with trimethylamine *N*-oxide dihydrate (TAO·2H₂O) afforded the corresponding PBd-*b*-PE and PS-*b*-PE copolymers (Scheme 4).²⁰ Both copolymers displayed narrow polydispersities ($\bar{D} < 1.14$) with a slightly higher molecular weight (24.0 kg mol⁻¹ and 11.9 kg mol⁻¹, respectively) than that of the theoretical value. The higher molecular weight observed indicates not all the 3-arm PBd (polybutadiene) or PS macroborane initiated the polyhomologation. The unreacted PBd and PS can be easily separated from the insoluble block copolymers in toluene at room temperature. Tri/tetra etc multiblock polymers can also be synthesized utilizing the same strategy but instead the homomacroanion is substituted by diblock, triblock and multiblock etc macroanions. More complex architectures can be synthesized by using living star homo/copolymers.

Scheme 4 One-pot synthesis of PE-based block copolymers by combining anionic polymerization and polyhomologation

In 2016, allyl-terminated PIBs (PIB-allyl) were synthesized by living cationic polymerization followed by *in situ* functionalization of the macrocation with allyltrimethylsilane. A 3-arm PIB star macroborane initiator can be obtained by reacting the terminal allyl substituted PIB with BH₃·THF. By adding sulfoxonium methylide to the preheated (80°C) solution of 3-arm PIB macroborane initiator, diblock copolymers PIB-*b*-PE were obtained after consumption of ylide monomer followed by oxidation/hydrolysis, $M_{n,NMR}$ ranging from 2.8–13.3 kg mol⁻¹ and dispersity ranging from 1.20–1.50 (Scheme 5).²¹

Scheme 5 Synthesis of block copolymer PIB-*b*-PE by combination of cationic polymerization and polyhomologation

2.2 Cyclic boranes (two or three active sites).

Polyhomologation initiated by cyclic borane has led to some special structures. For example, using 1-boraadamantane·THF as initiator, a three-arm star polymer with a cyclohexane as “junction point” was obtained after polyhomologation/oxidation/hydrolysis [Scheme 6, (1)].²² Another cyclic borane, derived from hydroboration of 1,5-hexadiene with the xylborane, initiated the polyhomologation of the methylide. After oxidation/hydrolysis of the macrocyclic the xylborane an α,ω -dihydroxypolymethylene was achieved [Scheme 6, (2)].²³ Macrocyclic ketones or tri(polymethylene) methanols can be prepared from the polyhomologated organoboranes using “stitching” transformation reactions (Scheme 7).^{23,24}

Scheme 6 Cyclic initiators for polyhomologation

Scheme 7 “Stitching” reactions of polyhomologated organoboranes

Recently, our group developed a “core-first” synthetic strategy for the synthesis of well-defined PE-based miktoarm star co/terpolymers

[Scheme 8, (1)].²⁵ 1,4-Pentadiene-3-yl 2-bromo-2-methylpropanoate was cyclic hydroborated with thexylborane, and used *in situ* as initiator to promote the polyhomologation of dimethylsulfoxonium methylide. An α,ω -dihydroxyl polyethylene (PE-OH)₂-Br ($M_{n,NMR} = 3.3$ – 32.9 kg mol⁻¹, $\bar{D} = 1.28$ – 1.59) was produced having at the middle of the chain a Br-initiating site for atom transfer radical polymerization (ATRP). A₂B 3-miktoarm star copolymers (PE-OH)₂-(PS-Br) ($M_{n,NMR} = 5.7$ – 57.8 kg mol⁻¹, $\bar{D} = 1.29$ – 1.49) were produced by ATRP of styrene. (PE-OH)₂-Br and (PE-OH)₂-(PS-Br) functionalized polymers were transformed to two new macroinitiators (PE-Br)₂-Br and (PE-Br)₂-(PS-Br) through esterification reaction and used for the synthesis of (AB)₂B [(PE-*b*-PS-Br)₂-(PS-Br), $M_{n,NMR} = 34.2$ kg mol⁻¹, $\bar{D} = 1.35$; (PE-*b*-PMMA-Br)₂-(PMMA-Br), $M_{n,NMR} = 10.5$ kg mol⁻¹, $\bar{D} = 1.40$] and (AC)₂(BC) [(PE-*b*-PMMA-Br)₂-(PS-*b*-PMMA-Br), $M_{n,NMR} = 41.4$ kg mol⁻¹, $\bar{D} = 1.41$] type 3-miktoarm star co/terpolymers. By using the same strategy, 4-arm stars (PE-OH)₄ ($M_{n,NMR} = 1700$ – 4000 g mol⁻¹, $\bar{D} = 1.20$ – 1.31), (PE-*b*-PCL)₄ ($M_{n,NMR} = 8980$ – 13430 g mol⁻¹, $\bar{D} = 1.24$ – 1.30), (PE-*b*-PMMA)₄ ($M_{n,NMR} = 45.6$ kg mol⁻¹, $\bar{D} = 1.55$) and PE-branched double-grafted block copolymer ($M_{w,GPC-LS} = 218$ kg mol⁻¹, $\bar{D} = 1.35$) (PCL: polycaprolactone, PMMA: polymethyl methacrylate) have been successfully synthesized through polyhomologation of ylides initiated by functionalized B-thexyl-silaboracycles [Scheme 8, (2)].²⁶

Scheme 8 Synthetic routes to PE-based A₂B, (AB)₂B, (AC)₂(BC), A₄, (AB)₄ and (AB)₂₄ star co/terpolymers

2.3 Monofunctional borane (One active site).

With design/synthesis of appropriate functional boranes, including polymeric boranes or cyclic boranes, the targeted PE-based polymers were successfully synthesized. But there are still some drawbacks, such as the sensitivity of borane compounds, as well as the use only

of thexyl as blocking group. Developing air stable borane compounds and exploring other blocking groups will be beneficial for the future development of PE-based macromolecular architectures. Our group recently found that a stable allylic borate can serve as initiator in polyhomologation of sulfoxonium methylide [Scheme 9, (1)].^{27a} By designing/synthesizing different allylic borate initiators, and using ¹H and ¹¹B NMR spectroscopy, we were able to show that only one site propagation of the ylide is possible through an allylic γ -migration stage. This new class of borate initiators fulfills the demand of stable initiator with two blocking groups. Meanwhile, catecholborane and its *in situ* derived monofunctional catecholboranes have also proved efficient initiators [Scheme 9, (2) and (3)].^{27b} The development of monofunctional borane initiators, on one hand, facilitates the synthesis of graft PE-based copolymers and on the other hand, could be a solution to the challenge of synthesizing poly(substituted methylenes) due to the reduced steric hindrance.

Scheme 9 Monofunctional borate initiators for polyhomologation

3. New ylide monomers

Although dimethylsulfoxonium methylide has been successful with organoboranes as initiators, the polyhomologation of substituted sulfoxonium ylides (the target mechanism is given in Scheme 10) is very important since such monomers offer the ability to play a key role in the development of new polyolefins, e.g. poly(methylmethacrylate) instead of polypropylene. Shea's group has investigated several substituted sulfoxonium ylides for polyhomologation as monomers (Scheme 11, A).¹³ Unfortunately, only (dimethylamino) phenyloxosulfonium methylide can be homopolymerized to produce PE with controlled molecular weight and narrow polydispersity (Scheme 11, B).²⁸ Other monomers, such as (dimethylamino)phenyloxosulfonium ethylide, (dimethylamino)-*p*-tolxyloxosulfonium cyclopropylide, and trimethylsilyl (TMS) diazomethane, can't homopolymerize in the presence of borane initiators, but can copolymerize with dimethylsulfoxonium methylide to form different random copolymers (Scheme 11, C).^{28–30}

It's probably due to the introduction of secondary or tertiary carbon at boron which increases the steric crowding at the boron center and decreases the reactivity toward the addition of the next ethyl/cyclopropylide. This proposed mechanism has been supported by comparison of molecular model of related boron analogues.^{13,29} In 2015, Shea's group developed a method to synthesize gradient ethylene-propylene copolymers by controlling the ratio of diethylsulfoxonium ethylide with dimethylsulfoxonium methylide (Scheme 11, D).³¹

Scheme 10 Target mechanism for the polyhomologation of substituted ylides with boranes

Scheme 11 Different ylide monomers in borane initiated polyhomologation

Significant efforts have been made to develop new ylide monomers in borane initiated polymerization. Mioskowski et al. discovered that allylic arsonium ylides could be employed in borane initiated polymerization. By changing the double bond substituent of the allylic arsonium ylides either C1 or C3 polymerization can occur. The 2-substituted allylic ylides mainly lead to C3 polymerization, while terminal unsubstituted monomers result in random C1/C3 polymerization (Scheme 12).^{32,33} In all cases, the polymerization involves a [1,3]-sigmatropic (or boratropic) rearrangement of the allylic boron intermediate.

Scheme 12 Allylic arsonium ylides used in borane initiated polymerization

Although the polymerization of terminal unsubstituted arsonium ylides^{32,33} is a good way to create polymers with unsaturated backbones, our group sought to investigate the effect of the terminal mono-substituted arsonium ylide in boron initiated polymerization. Moreover, the terminal substituted groups are more easily modified

than those located at the 2-position of the allyl group (Scheme 13, A). Furthermore, the combination of different monomers, such as sulfoxonium ylide and arsonium ylide, to achieve new PE-based copolymer is still a challenge. With this in mind, our group synthesized a terminal substituted arsonium ylides ω -2-methylallylarsonium ylide. It was found that polymerization of this monomer with triethylborane as initiator led to solely C3 polymerization. This can be explained as following: an ate complex, produced from ω -2-methylallylarsonium ylide and triethylborane, is rearranged to an allylic borane intermediate by losing triphenylarsine; then the terminal methyl substituted intermediate undergoes a [1,3]- σ rearrangement leading to isomeric allylic borane, which is involved in several cycles of reaction with the ylide eventually affording a C3 polymer after oxidation/hydrolysis. Furthermore, block and random copolymerization of this arsonium ylide with dimethylsulfoxonium methylide was successfully performed for the first time (Scheme 13, B).³⁴ These copolymer containing double bonds in the backbone, can potentially be transformed to other functional group or can act as initiating sites to grow side chains. Hence, developing different kinds of arsonium ylides, or combining them with sulfoxonium ylide in polymerization, is a promising way to synthesize unprecedented PE-based materials. Furthermore, whether selenonium ylide or tellurium ylide can be used as monomers in boron initiate polymerization still requires exploration (Scheme 13, C). Currently, we are working on these areas.

Scheme 13 Homopolymerization of terminal methyl substituted allylic arsonium ylides and copolymerization with dimethylsulfoxonium ylide initiated by triethylborane to afford C3/C1 copolymers

4. Combination of Polyhomologation with Other Polymerization Techniques

It is well known that the physical properties of polymers, such as density, crystallinity, diffusion rate, and mechanical strength, can be altered by varying the structure even at identical molecular weight. Polyhomologation is an ideal method to generate perfectly linear polyethylenes with a useful hydroxyl terminated group

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(triethylborane as initiator, Scheme 1). Post-functionalization or modification of PE-OH in combination with other polymerization techniques will provide a significant advantage to achieve different well-defined PE-based polymer architectures.

4.1 Combination with ring-opening polymerization (ROP).

The terminal hydroxyl group of PE-OH can serve as an initiator in ROP reactions. Ma's group utilized PE-OH as initiator and cyclic esters as monomers, such as ϵ -caprolactone (CL) or lactide (LA), to prepare PE-*b*-PCL (M_n ranging from 5400 to 13100 g mol⁻¹, $\bar{D}$ = 1.06-1.13) or PM-*b*-PLA (M_n ranging from 6200 to 13000 g mol⁻¹, $\bar{D}$ = 1.19-1.34) block copolymers (Scheme 14).³⁵ In addition, the formation of these copolymers are accompanied by the terminal OH-groups, which can be further transformed to multiblock polymers.

Scheme 14 Synthesis of block copolymers of PE-*b*-PCL or PE-*b*-PLA by using PE-OH as macroinitiator

4.2 Combination with atom transfer radical polymerization (ATRP).

ATRP has been proven as a powerful tool to synthesize a plethora of new materials with numerous applications.³⁶ The terminal hydroxyl group of PE-OH can react with 2-bromoisobutyryl bromide to afford a PE-Br macroinitiator for ATRP of acrylic, methacrylic and styrenic monomers in the presence of CuBr and *N,N,N',N',N''*-pentamethyldiethylenetriamine (PMDETA). Several PE-*b*-PS block copolymers with molecular weight from 5000 to 41800 g mol⁻¹ and $\bar{D}$ ranging from 1.10 to 1.23 were synthesized from PE-Br macroinitiators (M_n : 1900-1500 g mol⁻¹). The PE-Br macroinitiator was also employed to initiate the copolymerization of styrene and pentafluorostyrene (PFSt) leading to PE-*b*-P(St-co-PFSt) with molecular weight varying from 3500-12800 g mol⁻¹ and with narrow dispersity ($\bar{D}$ = 1.05-1.07). The same strategy was also employed to synthesize block copolymers PE-*b*-PMMA, PE-*b*-P^{*n*}BA and PE-*b*-P^{*n*}BA by using acrylic monomers. The corresponding copolymers are well-defined both in molecular weight and polydispersity (Scheme 15).³⁷

With appropriate modification of the PE-OH to dichloroacetyl terminated macroinitiator PE-Cl₂ ($M_{n, GPC}$ = 900 g mol⁻¹, $\bar{D}$ = 1.12), the two chlorides can be used to grow two PS or PMMA chains by ATRP. Two new well-defined PE-based AB₂ miktoarm star copolymers PE-*b*-(PS)₂ (M_n in the range of 5900-19200 g mol⁻¹, $\bar{D}$ in the range of 1.08-1.19) and PE-*b*-(PMMA)₂ (M_n ranging from 9000 to 13300 g mol⁻¹, $\bar{D}$ ranging from 1.25 to 1.30) were synthesized by this strategy (Scheme 15).^{37g}

These PE-based copolymers have been used to prepare highly ordered microporous films, micelles and compatibilizers for polymer blends.^{5,13} For instance, diblock copolymers PE-*b*-PS were employed in the breath-figure (BF) method procedure to fabricate polymer films (Figure 3). Honeycomb-like porous film with different average pore diameters were clearly observed, and the diameters depend on

molecular weight of PS segment. Another example is the morphology of miktoarm star copolymer PE-*b*-(PS)₂ with molecular weight 19200 g mol⁻¹ as shown in Figure 4. A wrinkle-like structure with nanopores (pore size = 100 nm, calculated value) on the surface was observed in the magnified SEM images (Figure 4, B and C).

Scheme 15. Synthesis of linear and miktoarm star copolymers from PE-based macroinitiators by using ATRP

Scheme 16 Synthesis of core cross-linked multiarm star polymers (A) (PE)_n-P(TPE-2St), (B) (TBDMSO-PE-*b*-PCL)_n-P(TPE-2St); (C) Photoluminescence (PL) spectra of (TBDMSO-PE-*b*-PCL)_n-P(TPE-2St) in THF/water mixtures with different water fractions measured at room temperature (23 °C) & Plot of I/I_0 versus water fraction in the THF/water mixture (I is PL intensity in THF/water mixtures with different water fractions; I_0 is PL intensity in pure THF solution; concentration, 0.1 g/L). Inset: photographs of THF/water mixtures of (TBDMSO-PE-*b*-PCL)_n-P(TPE-2St) with different water fractions taken under 365 nm UV illumination

Our group synthesized aggregation-induced emission (AIE) active core cross-linked multiarm star polymers, carrying PE, or PE-*b*-PCL arms, through an “arm-first” strategy, by atom transfer radical

copolymerization (ATRP) of a double styrene-functionalized tetraphenylethene (TPE-2St) used as a cross-linker with linear arm precursors fitted with terminal ATRP initiating moieties (Scheme 16, A & B).³⁸ Precursors made of TBDMSO-PE-*b*-PCL-Br diblocks were derived by combining polyhomologation with ring-opening polymerization (ROP). The extra -OH group of PE, present in ω -position in these PE samples were protected with *tert*-butyldimethylsilyloxyl (TBDMS) and could be used after deprotection for further modification. Since the cross-linked structure of the star restricts the intramolecular motions, the star polymers emitted strong fluorescence either in bulk or in solvent/non-solvent solutions (Scheme 16, C). In addition, due to the spherical shape, the star polymers exhibited temperature-responsive fluorescence.

Figure 3 SEM images of porous PE-*b*-PS films fabricated *via* casting/BF method at 20 °C in 50% RH. (a) PE_{2k}-*b*-PS_{10k}; (b) PE_{2k}-*b*-PS_{8k}; (c) PE_{2k}-*b*-PS_{5k}; (d) PE_{2k}-*b*-PS_{2k}. Copyright 2010, the Royal Society of Chemistry.^{37c}

Figure 4 SEM images of PE-*b*-(PS)₂ ($M_{n, GPC} = 19200 \text{ g mol}^{-1}$) electrospun particles using 2.5 wt% CHCl₃ solution at voltage of 11 kV, scale bar: (a) 50 μm; (b) 10 μm; (c) 5 μm. Copyright 2015, the Royal Society of Chemistry.^{37g}

4.3 Combination with reversible addition-fragmentation chain-transfer (RAFT) polymerization.

A RAFT chain-transfer agent PE-TTCB ($M_n = 700\text{--}3200 \text{ g mol}^{-1}$, $\bar{D} = 1.08\text{--}1.20$) was synthesized from hydroxyl terminated PE by reacting with S-1-dodecyl-S'-(α,α -dimethyl- α' -acetic acid) trithiocarbonate (DDAT),³⁹ and successfully used to initiate the controlled/living polymerization of styrene or 2-hydroxyethyl methacrylate (HEMA). A series of well-defined PE-*b*-PS ($M_n = 8200\text{--}34000 \text{ g mol}^{-1}$, $\bar{D} = 1.12\text{--}1.25$) or PE-*b*-P(St-co-HEMA) ($M_n = 8300\text{--}31300 \text{ g mol}^{-1}$, $\bar{D} = 1.12\text{--}1.29$) were obtained (Scheme 17).⁴⁰ The resulting PE-*b*-PS block copolymers were used to fabricate microfibers and microspheres by electrospinning process. The morphology of this block copolymer was strongly affected by the concentration of the copolymer (Figure 5). To be noted, the

copolymer PE-*b*-P(St-co-HEMA) has some hydroxyl groups which can serve initiating sites for the synthesis of graft copolymers.

Scheme 17 Synthesis of PE-*b*-PS diblock copolymers from PE-based macroinitiator using RAFT polymerization

Figure 5 SEM images of electrospun PE-*b*-PS (C1/RAFT) microspheres, microspheres-on-string, and microfibers obtained from PE-*b*-PS solutions in DMF-CHCl₃ with different polymer concentrations ($M_{n, PE-OH} = 1.4 \text{ kg mol}^{-1}$, $M_{n, PE-b-PS} = 27 \text{ kg mol}^{-1}$): (a) 5%, (b) 10%, (c) 15% and (d) 20% w/w, respectively. Copyright 2013, Wiley.^{40a}

4.4 Combination with ring-opening metathesis polymerization (ROMP).

ROMP has been employed in the synthesis of different polymers for several years.⁴¹ For example, Bowden and co-workers reported the production of several high molecular weight comb homopolymers and comb block copolymers containing polystyrene, polylactide and polynorbornene using ROMP.⁴² This method has also been employed to polymerize norbornyl-terminated syndiotactic polypropylene macromonomers to afford molecular brushes.⁴³ Although several molecular brushes have been synthesized,⁴⁴ there is no report concerning the synthesis of well-defined PE-based molecular brushes until the combination of polyhomologation with ROMP reported by our group.

Norbornyl macromonomers exhibit excellent performance in the synthesis of molecular brushes due to the high polymerizability of norbornene moieties driven by the high ring strain.⁴⁵ By esterification reaction of the PE-OH with 5-norbornene-2-carboxylic acid, a norbornyl macromonomer PE-Nor was successfully achieved. Then the norbornyl PEs (PE-Nor) were polymerized by ROMP in the presence of Grubbs catalyst (1st generation), PE molecular brushes were obtained in high conversions with M_n ranging from 50-190 kg mol⁻¹ and $\bar{D}$ ranging from 1.18-1.38, respectively (Scheme 18).⁴⁶ It should be noted that quantitative esterification of PE-OH is crucial in order to avoid the purification of the norbornyl

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macromonomer PE-Nor from its precursor PE-OH (Figure 6, A). A clear shift in high temperature GPC traces was observed after ROMP (Figure 6, B).

Scheme 18 Synthesis of well-defined PE molecular brushes by ROMP

Figure 6. A) PE-OH fully transform to norbornyl macromonomer as indicated by ^1H NMR; B) HT-GPC traces of Poly(PE₇₆₀)₆₃ molecular brush

Different PE-based random, block co-, ter- and quater molecular brushes as well as of bilayered or multilayered molecular brushes were synthesized by utilizing different norbornenyl macromonomers.⁴⁷ For example, the PE-Nor macromonomer (M_n : 700–1200 g mol⁻¹, $\bar{D}$: 1.05–1.06) was mixed with one, two or three other macromonomers (PCL-Nor, PEO-Nor and PS-Nor), after ROMP by using Grubbs 1st generation catalyst as initiator, different PE-based random molecular brush polymers (M_n : 75.5–213 kg mol⁻¹, $\bar{D}$: 1.06–1.19) were obtained (Scheme 19, A). The living behavior of ROMP and the good tolerance of Grubbs catalyst at high temperature give the opportunity to synthesize PE-based block molecular brushes (M_n : 65–250 kg mol⁻¹, $\bar{D}$: 1.06–1.19) through a sequential process (Scheme 19, B). The PE-based bilayered molecular brushes (M_n : 112–508 kg mol⁻¹, $\bar{D}$: 1.14–1.38) were synthesized according to the following steps: (1) PE-OH was used as a macroinitiator to polymerize ϵ -caprolactone in the presence of phosphazene base P2 as catalyst, (2) the resulting PE-*b*-PCL-OH was further functionalized with a norbornenyl group by esterification reaction to afford PE-*b*-PCL-Nor, (3) ROMP of diblock macromonomer PE-*b*-PCL-Nor led to the bilayered molecular brushes P(PE-*b*-PCL) (Scheme 19, C).

Based on the above initial and important discovery, two other well-defined molecular brushes, P(PE_{core}-*b*-PS_{corona}) and P(PE-OH) with internal PE blocks were also synthesized (Scheme 20).⁴⁸ For

P(PE_{core}-*b*-PS_{corona}), the following protocol was applied: (a) anionic polymerization of styrene followed by end-capping of polystyryllithium with 1,1-diphenyl ethylene (DPE) and quenched with allyl bromide to afford a PS-allyl polymer with molecular weight 1900 g mol⁻¹ (calculated by NMR, end group analysis); (b) hydroboration of the PS-allyl with BH₃, followed by polyhomologation/oxidation/hydrolysis to afford the OH-terminated

Scheme 19 Synthesis of PE-based molecular brushes by ROMP catalyzed by Grubbs catalyst

Scheme 20 Synthesis of well-defined molecular brushes A) P(PE_{core}-*b*-PS_{corona}) and B) P(PE-OH) with internal PE blocks

diblock copolymer PS-*b*-PE-OH; (c) esterification of PS-*b*-PE-OH with 5-norbornene-2-carboxylic acid to produce the macromonomer

PS-*b*-PE-Nor and ROMP using Grubbs 1st generation catalyst (Scheme 20, A). The same strategy was applied in the synthesis of hydroxyl functionalized PE molecular brushes, P(PE-OH) (Scheme 20, B). Thermal properties as well as solubility of the molecular brushes were studied in this work. The thermal properties of P(PE_{core}-*b*-PS_{corona}) and P(PE-OH), as well as of their precursors, were studied by differential scanning calorimetry (DSC). For P(PE_{core}-*b*-PS_{corona}), it was observed a decrease trend of melting temperature (T_m) from the macromonomer to molecular brush, due to the existence of the peripheral PS block which suppresses the movement of the PE chains. For P(PE-OH), the existence of hydroxyl groups in the periphery of molecular brushes increase the T_m , probably induced by inter- and intra-molecular hydrogen bonding.

4.5 Combination with Diels-Alder reaction or “Click” reaction.

A simple and effective method for the synthesis of PE-based diblock copolymers or triblock terpolymers was developed by our group through the Diels-Alder reaction.⁴⁹ The α -anthracene-PE-OH (diene 1), prepared by polyhomologation with tri(9-anthracenemethylpropyl ether)borane as initiator, reacted with furan-protected-maleimide-terminated PCL-MI or PEG-MI (dienophile) to afford PE₁₀₀-*b*-PCL₅₀ ($M_{n,NMR} = 6900 \text{ g mol}^{-1}$, $\bar{D} = 1.51$) or PE₁₀₀-*b*-PEG₁₀₀ ($M_{n,NMR} = 5600 \text{ g mol}^{-1}$, $\bar{D} = 1.14$) diblock copolymers (Scheme 21). Interestingly, the terminal hydroxyl group of α -anthracene-PE-OH could be further transformed to diblock copolymer Ant-PE-*b*-PLA-OH (diene 2) though ROP using lactide as monomer in the presence of DBU as catalyst. The obtained polymer Ant-PE-*b*-PLA-OH (diene 2) further reacts with dienophile PCL-MI or PEG-MI by “Diels-Alder” reaction, triblock terpolymer PLA-*b*-PE-*b*-PCL ($M_{n,NMR} = 9500 \text{ g mol}^{-1}$, $\bar{D} = 1.64$) or PLA-*b*-PE-*b*-PEG ($M_{n,NMR} = 8300 \text{ g mol}^{-1}$, $\bar{D} = 1.32$) was easily prepared (Scheme 21). The efficiency of Diels-Alder reaction ($DA_{eff}\% = 75\text{--}85\%$, calculated by UV-spectroscopy) indicated the power of this method to produce PE-based di- and triblock polymers.

Scheme 21 Synthesis of diblock copolymers and triblock terpolymers through the Diels-Alder reaction

Copper(I)-catalyzed azide-alkyne cycloaddition (CuAAC) “click” reaction can also be applied to construct PE-base architectures.

Recently, well-defined PE-based graft terpolymers PSt-*g*-(PCL-*b*-PE) were synthesized by “click” reaction (Scheme 22).⁵⁰ PE-*b*-PCL-alkyne was synthesized through esterification of PE-*b*-PCL-OH with 4-pentynoic acid. A random copolymer was obtained by nitroxide-mediated radical copolymerization (NMP) of styrene and 4-chloromethylstyrene. The modification of chloride to azido by reacting with sodium azide (NaN₃) generates a poly(St-*co*-4-AMS) containing many azido groups in the side chains. Then, random molecular brushes PSt-*g*-(PCL-*b*-PE) with varying molecular weight and narrow dispersity ($M_n = 32.9 \text{ kg mol}^{-1}$, $\bar{D} = 1.12$, and 56.6 kg mol^{-1} , $\bar{D} = 1.18$) were obtained by CuAAC “click” reaction of terminated alkyne group of PE-*b*-PCL-alkyne with side azido of poly(St-*co*-4-AMS).

Scheme 22 Synthesis of PE-based graft terpolymers through “click” reaction

PE-OH without modification can act as macroinitiators for ROP, or by post-modification of the -OH to appropriate initiating for ATRP, RAFT or macromonomers for ROMP, provides different well-defined PE-based polymers topologies. These new PE containing materials, almost impossible to synthesize by other existing techniques, could be potential candidates for new applications.

5. Conclusion and Future Outlook

In summary, borane initiated living polyhomologation provides a new way to achieve different PE-based polymers. By rational design and synthesis of boranes or ylide monomers, different functional polyethylenes can be easily achieved. Further post-functionalization of hydroxyl terminated polyethylene and combination with other polymerization methods, results in different PE-based polymer architectures.

As it stands, challenges remain in borane initiated polymerization with the most significant drawback being the ylide monomers themselves, since these materials are not commercially available and their synthesis non trivial. Furthermore, only a small part of the ylide contributes in the chain formation. Additional complexity comes from the sensitivity of borane initiators to oxygen, with the danger as part of them may be oxidized during or before the polymerization. Consequently, the development of new non sensitive polyhomologation initiators is a priority.

The greatest challenge however is to find the appropriate initiator/ylide combination to produce poly(substituted methylene)s. Until now, the borane-initiated polymerization is limited to ylides of sulfur (group six element) and arsenic (group five element) monomers it might be useful, to study other ylides, such as ammonium, phosphorus, oxonium, selenium and tellurium. The exploration of these ylide monomers will open new horizons towards

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new polymers with unprecedented architectures and properties, which will be limited only by our imagination.

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