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## Boron “Stitching” Reaction: A Powerful Tool for the Synthesis of Polyethylene-Based Star Architectures

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**The linking of macroanions with  $\text{BF}_3\text{OEt}_2$  leads to a 3-arm star with boron junction point, which can serve as macroinitiator for the polyhomologation of dimethyl sulfoxonium methylide and thus enabling the synthesis of novel but not “stable” polyethylene (PE)-based 3-arm star block copolymers. Taking advantage of the “stitching” reaction, which transforms the “unstable” boron junction to “stable” carbon, we were able to synthesize novel star block copolymers. This strategy is general and opens new horizons towards unprecedented PE-based materials.**

The design/synthesis/properties of novel macromolecular architectures is always of high demand in academia and industry, since it contributes to the ultimate goal of Polymer Science, which is the production of polymers with predetermined properties. In particular, in the case of polyethylene (PE) it is necessary, since it is and will continue to be the most widely used industrial polymer in the world, benefiting from its product versatility, hydrophobicity, mechanical strength, flexibility, resistance to the harsh environment, easy processability, recyclability, along with low cost.<sup>1</sup>

So far, well-defined star polyethylenes have been synthesized either by hydrogenation of anionically prepared polybutadiene (1,4 microstructure) stars<sup>2,3</sup> or by catalytic “living” coordination polymerization.<sup>4</sup> In the case of “living” catalytic ethylene polymerization, Ye and his group were the first to report the synthesis of symmetric 3-arm star PEs using a trinuclear Pd-diimine complex.<sup>5</sup> The same group has extended this strategy to more complex architectures such as hyperbranched and core-cross linked multi-arm stars.<sup>6-9</sup> Unfortunately, while the polydispersity in the above methods is narrow ( $\text{Đ} < 1.15$ ) the PEs is branched.

In 1997, Shea launched a boron catalyzed/initiated polymerization of dimethylsulfoxonium methylide, where the resulting perfectly linear and low polydispersity polymethylene (equivalent to polyethylene, PE) chain is built by one carbon at a time (C1 polymerization), he coined such polymerization “polyhomologation”.<sup>10-13</sup> The use of different functionalized ylides and/or versatile organoborane initiators (mono-, di- and tri-functional) and with the synergy of other living and controlled/living polymerization methods enabled the synthesis of well-defined PE-based block copolymers, as well as complex structures such as miktoarm stars, cyclics, tadpoles, etc.<sup>14-26</sup>

A source of inspiration towards this direction is certainly the organic chemistry.<sup>27-29</sup> Organoboron chemistry has been used extensively in organic synthesis for more than sixty years and lately in polymer chemistry.<sup>30-32</sup> Shea and coworkers have already used a boron transformation reaction (stitching) to synthesize 3-arm star PE homopolymers.<sup>33</sup>

In this work, we report a one-pot strategy for the synthesis of perfectly linear PE-based star block copolymers (BCPs) by combining anionic polymerization, polyhomologation and “stitching” chemistry. It involves the following steps: (a) linking of anionically synthesized macroanions with  $\text{BF}_3\text{OEt}_2$  to afford boron-linked 3-arm stars (macroinitiator), (b) *in situ* polyhomologation of dimethylsulfoxonium methylide and (c) “stitching” transformation of the “unstable” boron to “stable” carbon atom, followed by oxidation/hydrolysis to produce 3-arm PE-based star block copolymer (Scheme 1). This study shows that “stitching” in combination with polymer chemistry, is a powerful tool for the synthesis of polymers with star topology but not only.

Boron-linked 3-arm star polystyrenes and polyisoprenes were prepared (high vacuum techniques, Figure S1) by linking living macroanions (20 % excess) with  $\text{BF}_3\text{OEt}_2$  and used without isolation as macroinitiators for the polyhomologation of dimethylsulfoxonium methylide (Scheme 2).<sup>34</sup> Similar to chlorosilane linking chemistry, an excess of the living precursor was required to drive the reaction to completion.<sup>35</sup> GPC traces of  $\text{PS}_3\text{B}$  (Figure 1,a2) and  $\text{PI}_3\text{B}$  (Figure S2,a2) do not correspond to the original 3-arm star polymer peaks due to the detachment of one, two and three arms from the highly air (humidity, oxygen) boron junction (see Fig. S3 in SI).

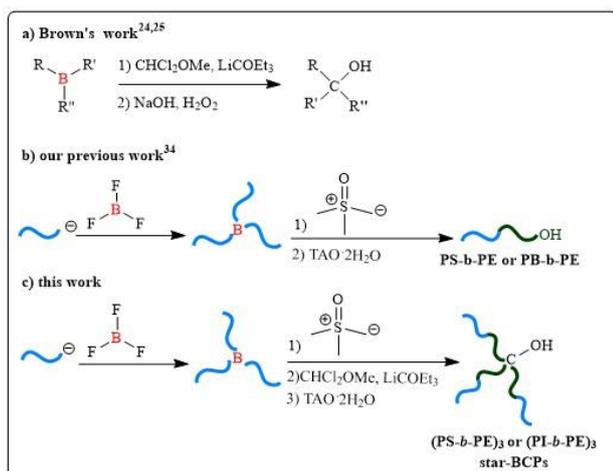
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**Scheme 1** a) Brown's "stitching" reaction in small organoboranes, b) combination of anionic polymerization and polyhomologation through  $\text{BF}_3$  "bridge molecule" and c) combination of anionic polymerization, polyhomologation and "stitching" reaction.

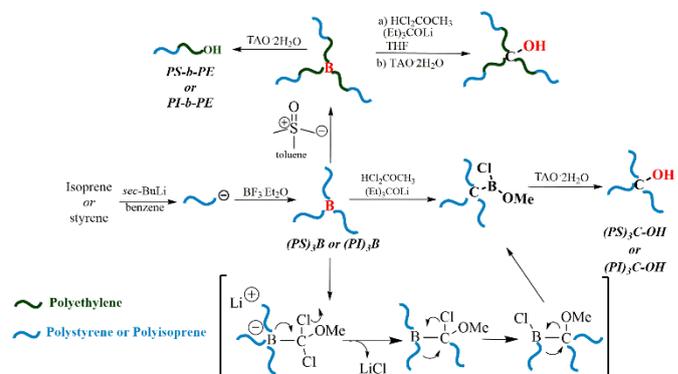
**Table 1.** Molecular characterization results of 3-arm star homopolymers and star block copolymers after "stitching" reaction

entry	Sample	Linear precursor				Star	
		$M_{n,\text{GPC}}$ (kg/mol) PI or PS	$\bar{D}$ $M_w/M_n$	$M_n^{\text{H-NMR}}^c$ (kg/mol)	$f_{(\text{PE})}^c$ wt %	$M_{w,\text{GPC}}$ (kg/mol)	$\bar{D}$
1	(PI-1) <sub>3</sub>	6.4 <sup>a</sup>	1.04 <sup>a</sup>	-	-	17.8 <sup>a</sup>	1.08 <sup>a</sup>
2	(PI-2) <sub>3</sub>	2.3 <sup>a</sup>	1.06 <sup>a</sup>	-	-	6.1 <sup>a</sup>	1.09 <sup>a</sup>
3	(PS-1) <sub>3</sub>	1.1 <sup>a</sup>	1.07 <sup>a</sup>	-	-	3.1 <sup>a</sup>	1.09 <sup>a</sup>
4	(PS-2) <sub>3</sub>	20.5 <sup>a</sup>	1.05 <sup>a</sup>	-	-	58.0 <sup>a</sup>	1.11 <sup>a</sup>
5	(PS- <i>b</i> -PE) <sub>3</sub>	11.8 <sup>b</sup>	1.09 <sup>b</sup>	14.2 (PS), 32.1 (PE)	70	97.0 <sup>d</sup>	1.15 <sup>b</sup>
6	(PI- <i>b</i> -PE) <sub>3</sub>	6.8 <sup>b</sup>	1.10 <sup>b</sup>	8.2 (PI), 2.4 (PE)	23	23.7 <sup>d</sup>	1.14 <sup>b</sup>

<sup>a</sup>GPC (THF, 35 °C). <sup>b</sup>HT-GPC (1,2,4-trichlorobenzene, 150 °C), <sup>c</sup> $M_n^{\text{H-NMR}}$  and  $f_{(\text{PE})}$  were calculated from <sup>1</sup>H-NMR spectra using the area ratio of protons in terminal  $-\text{CH}_2\text{OH}$  at  $\delta = \sim 3.5$  ppm to the ones on the backbone. <sup>d</sup> $M_{w,\text{GPC}}$ , determined by triple-detection HT-GPC.

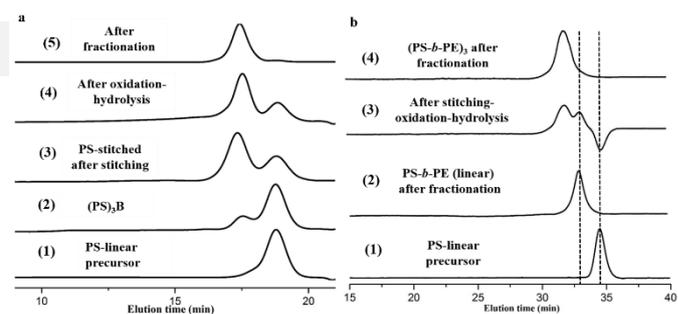
Initially, the "stitching" reaction was performed on  $\text{PS}_3\text{B}$  or  $\text{PI}_3\text{B}$  3-arm stars resulting in tris(polystyrene)methanol ( $\text{PS}_3\text{C-OH}$ ) and tris(polyisoprene)methanol ( $\text{PI}_3\text{C-OH}$ ) (Scheme 2). More specifically, the deprotonation of dichloromethyl methyl ether (DCME) by the hindered base forms an anion that attacks the electrophilic boron atom, of the boron-star polymers, resulting in a 'ate' complex. Then, three sequential intramolecular migrations occur to afford a 3-arm star with a tertiary alcohol at the junction point, after oxidation/hydrolysis. By screening the reaction conditions, it was found that treating  $\text{PS}_3\text{B}$  or  $\text{PI}_3\text{B}$  with 5.5 eq. of DCME and 5.0 eq. of  $(\text{Et})_3\text{COLi}$  in THF at 25 °C generates the higher yield of tertiary alcohol, rather than the 1/1.1/1 ratio, reported for low molecular weight equivalent tralkylboranes.<sup>36</sup> Several experiments were failed to

initiate a new polymerization directly from the  $-\text{OH}$  group (ring opening polymerization of  $\epsilon$ -caprolactone) or indirectly after esterification with  $\alpha$ -bromoisobutyryl bromide (atom transfer radical polymerization), probably due to steric constraints. It should be mentioned that "stitching" could be also performed by carbonylation but is difficult to be implemented in polymer synthesis.<sup>25,37</sup>



**Scheme 2** Synthetic routes to linear diblock copolymers and 3-arm stars combining anionic polymerization, polyhomologation and "stitching" reaction.

GPC traces (Figure 1,a3 and Figure S2,a3) revealed efficient linking and "stitching" reaction as indicated by the appearance of a new elution peak of higher molecular weight species (lower elution time). The peak corresponding to lower molecular weight (higher elution time) is attributed to the excess of linear precursor, intentionally added to drive the linking to completion. The small shoulder (Figure S4, dash line) with double molecular weight is ascribed to two-armed coupled product, probably due to incomplete triple 1,2 migration ( $\sim 65\%$ ) from boron to carbon (steric hindrance).<sup>27,37</sup> Another possible explanation is the partial linking reaction of "living" macroanions and  $\text{BF}_3\text{OEt}_2$ . Direct evaluation of the linking-reaction is not easily attainable, due to the sensitivity of macroboron species.



**Fig. 1** Monitoring the synthesis/fractionation by GPC of a)  $(\text{PS})_3\text{C-OH}$  (entry 3) in THF 35 °C and b)  $(\text{PS-}b\text{-PE})_3\text{C-OH}$  (entry 5) in TCB at 150 °C. Note:  $(dn/dc)_{\text{PS}} > 0$  in both THF and TCB and  $(dn/dc)_{\text{PE}} < 0$  in TCB at 150 °C. The traces (2), (3), (4) in **b** are inverted for better visualization and comparison.

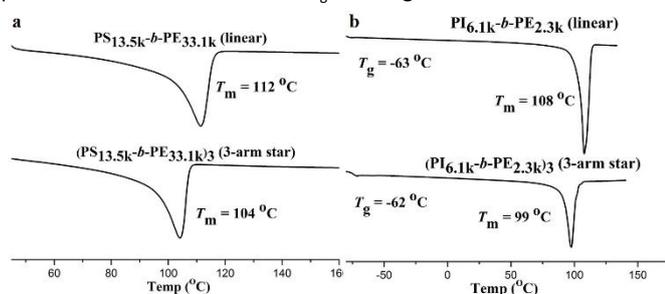
Further evidence of the 3-arm star formation was provided by the Mark-Houwink plot (Figure S5). It is clear that, for the same molecular weight, linear PS (black dots) has higher intrinsic viscosity (more extended structure) compared to the 3-arm PS sample (compact structure). Same trend was shown for the PI stars too.

Trimacromolecular boranes ( $\text{PS}_3\text{B}$  and  $\text{PI}_3\text{B}$ ) were used as initiators for the "living" polyhomologation of dimethylsulfoxonium

methylide in one-pot process. The resulting (PS-*b*-PE)<sub>3</sub>B and (PI-*b*-PE)<sub>3</sub>B solution were either oxidized/hydrolyzed with trimethylamine-N-oxide dihydrate (TAO·2H<sub>2</sub>O) to afford linear PS-*b*-PE/PI-*b*-PE or converted to (PS-*b*-PE)<sub>3</sub>C-OH/(PI-*b*-PE)<sub>3</sub>C-OH 3-arm BCPs by “stitching” reaction followed by treatment with TAO·2H<sub>2</sub>O. For both linear PE-based samples (Table 1, entries 5,6), a monomodal peak appeared at higher molecular weight, indicating successful polyhomologation (Figure 1,b2 and Figure S2,b2). The peak attributed to the excess of linear precursor was eliminated by centrifugation in toluene. GPC traces for the 3-arm BCPs, after “stitching” reaction, revealed the same trend with the above mentioned 3-arm star homopolymers but with, a lower yield. Apparently, lower yield was obtained due to the use of benzene/toluene mixture as reaction solvent instead of THF (poor PE solubility).

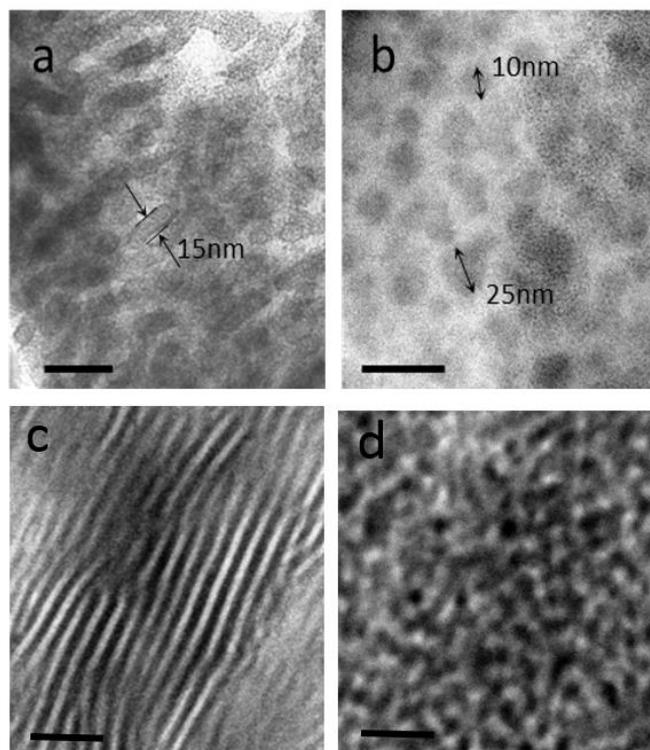
As shown in Figure S6, the PE fingerprint in (PI-*b*-PE)<sub>3</sub>C-OH 3-arm BCPs and PI-*b*-PE linear BCPs was obvious in the <sup>1</sup>H-NMR spectra with the characteristic chemical shift of PE at  $\delta = 1.4$  ppm (-CH<sub>2</sub>-). For the linear counterparts, the chemical shift of -CH<sub>2</sub>- protons connected to hydroxyl group (-CH<sub>2</sub>-OH) is at  $\delta = 3.3$  ppm and the signal assigned to the protons of PI block appears at  $\delta = 4.8$ -5.5 ppm. By end-group analysis, the ratio of PE component in the corresponding diblock copolymer and the degree of polymerization for each block (DP<sub>PE</sub> = 86 and DP<sub>PI</sub> = 124) were calculated.<sup>38</sup> Comparing to the linear diblock copolymer, the peak at  $\delta = 3.3$  ppm disappeared in the spectrum of star block (Figure S6, down) due to the lack of protons in the tertiary carbon connected to the hydroxyl group. A same observation was made for the (PS-*b*-PE)<sub>3</sub>C-OH sample (Figure S7).

The melting behavior of the linear diblock copolymers along with the corresponding 3-arm stars was studied by differential scanning calorimetry (DSC) analysis and the thermal traces are given in Figure 2. The linear PS-*b*-PE exhibits melting temperature ( $T_m$ ) 112 °C for PE and 19.5% crystallinity, while the glass transition temperature ( $T_g$ ) of PS segment was hidden by the melting trace of PE block. In the case of (PS-*b*-PE)<sub>3</sub> 3-arm star BCPs the  $T_m$  was 104 °C and the crystallinity decreased to 17%, likely due to the reduced PE chain mobility and the crystal structure irregularity resulting from the star architecture. Linear PI-*b*-PE and the corresponding 3-arm star (PI-*b*-PE)<sub>3</sub> showed  $T_m$  at 108 °C and 99 °C along with 15% and 13% crystallinity, respectively. The decrease in crystallinity, compare to the (PS-*b*-PE)<sub>3</sub>, is attributed to the lower chain length of the PE block. For both linear and 3-arm star copolymers, an endothermic peak around -63 °C ascribed to  $T_g$  of PI segment was observed.



**Fig. 2** DSC curves of (a) PS-*b*-PE and (b) PI-*b*-PE for linear and 3-arm star counterparts respectively.

The presence of crystalline blocks in the copolymers introduces extra complexity to their final morphology compared to fully amorphous polymers. Here, the melt structure is governed by two competing self-organizing mechanisms: crystallization and microphase-separation. Electron micrographs of stained (OsO<sub>4</sub> for PI-*b*-PE and RuO<sub>4</sub> for PS-*b*-PE) sections revealed different morphologies for linear and 3-arm systems. Confined crystallization for PS-*b*-PE ( $T_g^{PS} > T_m^{PE}$ ) and break-out crystallization for PI-*b*-PE ( $T_g^{PI} < T_m^{PE}$ ) take place.<sup>39,40</sup> Elongated morphologies (cylinders/lamellae) with roughly 15 nm thickness are observed for linear PS-*b*-PE (Figure 3a), consistent with the expected morphology of linear block copolymers with volume fractions  $f_{PE}=0.7$  and  $f_{PS}=0.3$  before and after confined crystallization. In contrast, the 3-arm architecture may favour the formation of radial morphologies which is shown by PS spheres of the 3-arm PS-*b*-PE with size range of 10-25 nm (Figure 3b). In contrast to PS, PI weakly confines the crystallization of PE (favouring the formation of lamellar morphologies), thus new morphologies are driven by the crystallization of the PE domain, which favours the formation of lamellar morphological structures.<sup>41</sup> Indeed, lamellar morphologies were observed for linear PI-*b*-PE (Figure 3c) with domain spacing of around 20 nm. However, disordered and branched lamellar structures (possibly interconnected) were observed for 3-arm PI-*b*-PE (Figure 3d). During crystallization, the 3-arm architecture results in random branching of crystal lamellae by the third arm which serves as nucleation sites for subsequent crystallization, with the final morphology being the branched crystal lamellae structures in Figure 3d.



**Fig. 3** TEM images of a) PS-*b*-PE block copolymer, b) (PS-*b*-PE)<sub>3</sub> star-block copolymer, c) PI-*b*-PE block copolymer and d) (PI-*b*-PE)<sub>3</sub> star-block copolymer. Scale bar represents 50 nm.

In summary, a novel strategy toward well-defined PE-based 3-arm star block copolymers was developed by combining two living polymerization methods (anionic polymerization and polyhomologation) with a transformation reaction known as “stitching”. Initially, a “living” macroanion (PS<sup>-</sup>Li<sup>+</sup> or PI<sup>-</sup>Li<sup>+</sup>) was reacted with BF<sub>3</sub>OEt<sub>2</sub> to afford PS<sub>3</sub>B or PI<sub>3</sub>B trimacromolecular boranes. Subsequent polyhomologation of dimethylsulfoxonium methylide led to the formation of (PS-*b*-PE)<sub>3</sub>B or (PI-*b*-PE)<sub>3</sub>B, while after “stitching”-oxidation/hydrolysis, (PS-*b*-PE)<sub>3</sub>C-OH or (PI-*b*-PE)<sub>3</sub>C-OH 3-arm star block copolymers were synthesized. Preliminary TEM studies on bulk morphology revealed structures with increased crystallization frustration for the 3-arm star copolymers compared to its linear counterparts. Future challenges include the design/synthesis of more sophisticated boron compounds as initiators or linking agents to produce PE-based complex macromolecular architectures such as H, comb, cyclic, dendritic, etc.

### Conflicts of interest

There are no conflicts to declare.

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