A novel one-pot methodology combining anionic polymerization and polyhomologation, through a “bridge” molecule (BF$_3$OEt$_2$), was developed for the synthesis of polyethylene (PE)-based block copolymers. The anionically synthesized macroanion reacts with the “bridge” molecule to afford a 3-arm star (trimacromolecular borane) which serves as an initiator for the polyhomologation.

Polyethylene (PE)-based materials are very important to modern life covering a wide spectrum of applications from commodity plastics (e.g. packaging, bottles) to precision-processed biomaterials (e.g. total joint replacement and medical devices). In order to better understand the behaviour and improve the performance of these materials, well-defined (controllable molecular weight, narrow molecular weight and structural distribution) PE-based polymers are needed. Unfortunately, anionic polymerization which gives access to well-defined polymers when chain growth occurs in a “living” fashion is not compatible with ethylene, the monomer of PE. The only way to prepare well-defined PEs by anionic polymerization is by hydrogenation of the corresponding anionically prepared PBd-1,4. However, the produced PE possesses butylene units originating from the hydrogenation of the unavoidable 1,2-units (minimum 5%) formed during the chain growth. Recently, Shea developed a novel polymerization methodology leading to perfectly linear PEs. The general reaction scheme involves the formation of an organoboron zwitterionic complex between a methylene (monomer) and a triallylborate Lewis acid (initiator) which breaks down by the intramolecular 1,2-migration. As a consequence, the methylene group of methyle is randomly inserted one by one into the three branches of the triallylborate leading to a 3-arm PE star. The resulting star is subsequently oxidized/hydrolysed to give perfectly OH-end-capped linear PEs. Molecular weights from 500 to 5.0 × 10$^2$ and the polydispersity index (PDI) typically less than 1.1 have been reported. For this type of polymerization Shea coined the name polyhomologation or C1 polymerization.

By using functionalized ylides and/or organoboranes, functionalized linear and nonlinear homo/copolymers, such as α-hydroxyl-α-allylic PE, 3-armed α-hydroxyl PE star, PE-α-PP(polypropylene) and cyclic PE have been synthesized. Until now, polyhomologation has been combined with controlled/living radical and ring opening polymerization reactions to afford PE-based block copolymers such as PS-b-PE, PEO-b-PE diblock and PE-b-PDMS-b-PE triblock copolymers, etc. (PS: polystyrene; PEO: polyethylene oxide; PDMS: polydimethylsiloxane).

Here, we report a novel one-pot methodology combining anionic polymerization and polyhomologation, through a “bridge” molecule (BF$_3$OEt$_2$), for the synthesis of polyethylene (PE)-based block copolymers. The synthetic approach involves: (a) the synthesis of a 3-arm star polymer (trimacromolecular borane, macroinitiator) by reacting living macroanions with BF$_3$OEt$_2$, (b) the in situ polyhomologation of dimethylsulfoxonium methide, with the macroinitiator to produce a 3-arm star block copolymer of PE, and (c) the oxidation/hydrolysis by trimethylamine N-oxide dihydrate (TAO) to afford the PE-based block copolymers. As examples the syntheses of PBd-b-PE (PBd: polybutadiene) and PS-b-PE are shown in Scheme 1. The details are given in the ESL.

A living macroanion, PBdLi or PSLi, was first synthesized in cyclohexane at room temperature and then reacted (30% excess) with BF$_3$OEt$_2$ (0.7 M solution in diethyl ether) to afford a 3-arm boron-linked star. Due to the high sensitivity

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Scheme 1 Combination of anionic polymerization and polyhomologation leading to PBd-b-PE and PS-b-PE block copolymers (BF$_3$OEt$_2$ “bridge” molecule).
Table 1 PE-based block copolymers synthesized by combining anionic polymerization and polyhomologation

<table>
<thead>
<tr>
<th>Sample</th>
<th>PBD or PS block</th>
<th>PE block</th>
<th>(PBD or PS)-b-PE</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>$M_n$ ($\times 10^4$)</td>
<td>$P_{D_{1,SEC}}$</td>
<td>$M_{n,NMR}$</td>
</tr>
<tr>
<td>PBD-b-PE</td>
<td>5.90</td>
<td>1.05</td>
<td>3.80</td>
</tr>
<tr>
<td>PS-b-PE</td>
<td>6.50</td>
<td>1.09</td>
<td>3.30</td>
</tr>
</tbody>
</table>

a The molecular weight was determined by MALDI-ToF (Fig. S1, ESI). b The molecular weight was determined by HT-SEC using TCB as an eluent at 150 °C with a flow rate of 0.8 mL min$^{-1}$ calibrated by PS standards. c The molecular weight was calculated from the ratio of the ylide to the initiator. d $M_{n,NMR} = 14 \times DP_{PBD} \times (\delta_{4.8–5.6ppm} - 0.6 \times \delta_{6.4–7.4ppm} - 2 \times \delta_{4.8–5.6ppm} \times \delta_{6.4–7.4ppm})$. e $M_{n,PS,NMR} = 14 \times DP_{PS} \times (\delta_{4.8–5.6ppm} - 0.6 \times \delta_{6.4–7.4ppm} \times \delta_{4.8–5.6ppm})$. f The glass transition of the PS block was hidden by the melting process of the PE block. g Upper critical solution temperature (UCST) was measured in toluene (3 mg mL$^{-1}$) on a UV-Vis instrument with a manual temperature controller.

It is clear that the peak appearing after polyhomologation moves to the higher molecular weight region (lower elution volumes), the lower molecular weight peak corresponding to the excess precursor eliminated after fractionation. For this reason the polyhomologation products were dissolved in toluene at high temperature to give a clear and transparent solution, followed by cooling to room temperature. The solution was then centrifuged in the presence of a small amount of selective solvent for PBD (petroleum ether) and PS (acetone) to facilitate the separation. The absence of the PBD and PS precursors (Fig. 3) proves the success of the fractionation (Table 1).

Successful syntheses of diblock copolymers have been confirmed by Fourier-transformed infrared spectroscopy (FTIR) (Fig. 4). In the case of PBD-b-PE, the peaks at 964 and 910 cm$^{-1}$ characteristic of and attributable to $\equiv$C–H bending vibration in PBD blocks were found.

In the DSC curve (Fig. 5) of the PBD-b-PE diblock copolymer, a melt temperature of 101 °C attributable to the PE block was...
found, as well as the glass transition to the PBd block at ca. −85 °C. In the case of PS-b-PE, the glass transition of the PS block was covered by the melting process of the PE block.

The PE fingerprint is clearly seen from the thermal behavior of the PE copolymers in toluene monitored by UV-Vis measurements at 450 nm. The graphs (transmittance as a function of temperature) of PBd-b-PE and PS-b-PE are shown in Fig. 6. A phase transition occurs at 40–55 °C upon heating the PBd-b-PE solution (3 mg mL⁻¹) - the transition then increases from ~40% to 100%. For PS-b-PE, the phase transition is much more significant as the transmittance increases from 2% to 100% upon increasing the temperature to 40–55 °C.

The PE fingerprint was also evident in the thermal responses (shielding effect) of diblock copolymers in ¹H NMR spectra (Fig. 6). The single and sharp peak at 1.4 ppm, attributable to the protons in PE backbone, compared to vinyl protons in the 1,4-type double bond in the PBd block at 5.5 ppm, increases with temperature, which means that more and more PE blocks dissolved in the solvent. The area ratio of the peaks at 1.4 ppm to the one at 4.8–5.6 ppm was used to calculate the ratio of the PE block in the copolymers using:

\[ M_{PBd-PE,\text{NM}} = 14 \times DP_{PBd} \times (A_{1.4,2.4ppm} - 0.6 \times A_{1.4,7,14ppm} - 2 \times A_{4.8,5.6ppm})/A_{1.4,2.4ppm} \]

Correspondingly, the peaks of aryl protons due to the PS blocks at 6.4–6.9 ppm were employed to calculate the respective contents of PS and PE in PS-b-PE copolymers. Surprisingly, the molecular weights calculated in this way were higher than expected. For PBd-b-PE, the molecular weight of 2.4 × 10⁵ drawn from NMR for the PE block is 2.3 times higher than the expected value of 10.5 × 10⁴. The deviation is more obvious for PS-b-PE (Table 1). The higher molecular weight observed indicates that the macroinitiator concentration was lower than the theoretical one, meaning that the efficiency of the linking reaction (living polymers with BF₃OEt₂) was about 30%. Other reasons for this disagreement in molecular weights should be excluded since the PDIs of the final block copolymers were very low (Table 1).

In conclusion, a novel strategy, based on anionic polymerization combined with polyhomologation through a “bridge” molecule (BF₃OEt₂), has been proposed for the synthesis of PE-based block copolymers. The examples described in this work (PBd-b-PE and PS-b-PE) are only two out of the many that can be prepared by this general methodology. A few are given below: ABE, (AB)₂or three CE, (ABC)₂or three DE, ABCDE, (ABCD)₂or three FE, etc. (A, B, C, D, E: different blocks, F: polyethylene). The potential of this method is limited only by our imagination.

Notes and references


