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Complex Star Architectures of Well-Defined Polyethylene-based Co/Terpolymers

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ABSTRACT: Well-defined polyethylene (PE)-based 3-miktoarm star copolymers (PI\textsubscript{2}PE-OH, PI\textsubscript{2}(PI’-b-PE)-OH and terpolymer PI\textsubscript{2}(PS-b-PE)-OH (PI: polyisoprene, PS: polystyrene), bearing a functional group (–OH) at the PE chain-end, were synthesized by combining anionic polymerization, polyhomologation and linking reaction with a “bridge” molecule, BF\textsubscript{3}OEt\textsubscript{2}. 4-(Dichloromethylsilyl)diphenylethylene (DCMSDPE) was first synthesized and linked with anionically prepared linear PI, through titration, to afford the “living” star precursors. Subsequently, boron-linked macroinitiators were synthesized through linking reaction with BF\textsubscript{3}OEt\textsubscript{2} for the polyhomologation of dimethylsulfoxonium methylide to produce novel PE-based miktoarm star polymers. All intermediates and final products were characterized by high temperature size exclusion chromatography (HT-SEC), proton nuclear magnetic resonance spectroscopy (\textsuperscript{1}H-NMR) and differential scanning calorimetry (DSC). The microdomain morphologies of the samples...
were elucidated by transmission electron microscopy (TEM) imaging of microtomed sections as well as small-angle and wide-angle x-ray scattering (SAXS, WAXS) as a function of sample temperature. Depending on the relative degree of segregation (varying with block molecular weight and the interaction parameter between blocks) versus the crystallization temperature of the PE block, both crystallization-driven microphase separation and segregation-driven order-disorder microphase separation can take place, resulting in various domain morphologies.

INTRODUCTION

Polyethylene (PE)-based materials cover a wide range of applications from commodity plastics (packaging, bottles, containers) to precision-processed biocompatible materials (total joint replacement and medical devices) and have a high impact in modern life.\textsuperscript{1} The versatility of PE-based materials originates from their properties including thermal stability, mechanical strength, and toughness, low cost, ability to tune crystallinity and thus properties, easy processability and flexibility.\textsuperscript{2} The development of new architectures of well-defined PE-based polymers will improve the performance and broaden the applications of these materials, since polymer properties (elasticity, density and viscoelastic behavior) are highly influenced by polymer macromolecular architectures.\textsuperscript{3} Therefore, studies focusing on the synthesis of well-defined PE-based polymer architectures (e.g., star polymers) are of increasing interest.

Miktoarm star polymers (from the Greek word \textit{μικτός}, meaning mixed), a term coined by the Hadjichristidis’ group in the early ’90s, refer to stars with chemical asymmetry (chemically different arms).\textsuperscript{4} This type of polymers have attracted significant attention in past decades, due to their unique chemical structure, novel physical attributes and microdomain morphologies.\textsuperscript{5-9} The most efficient (in minimizing molecular and structural heterogeneity) synthetic method for miktoarm stars is anionic polymerization \textit{via} high vacuum techniques and the utilization of appropriate linking agents such as chlorosilanes, divinylbenzenes or double 1,1-diphenylethenes.\textsuperscript{10} Using anionic polymerization in combination with chlorosilane chemistry, PE-based star polymers were obtained through the synthesis of polybutadiene
(PBd) stars followed by hydrogenation. Unfortunately, the PEs synthesized by this method are contaminated with ~7% butene units due to 1,2-microstructure of PBd (93% 1,4- and 7% 1,2-content)\textsuperscript{11,12} and such local branches inhibit the degree of crystallinity, lower the melting point and result in less robust mechanical properties.

Another synthetic strategy for well-defined PE-based star polymers is by “living” catalytic ethylene polymerization. Specifically, a trinuclear Pd-diimine complex was used for the direct “living” polymerization of ethylene to afford well-defined 3-arm star PE, containing a backbone of linear topology bearing short branches.\textsuperscript{13} Moreover, miktoarm star polymers were generated through the synthesis of hydroxyl-terminated PE followed by “click” chemistry, atom transfer radical polymerization (ATRP) or ring-opening polymerization (ROP).\textsuperscript{14-16} A drawback of catalytic ethylene polymerization is the lack of efficiency to produce end-functionalized PEs, which act as intermediates for the synthesis of miktoarm star polymers in combination with other polymerization techniques.\textsuperscript{17} Therefore, it is clear that the development of an alternative controlled/living polymerization method to synthesize well-defined PE is essential.

Polyhomologation, discovered by Shea and coworkers, is an alkylborane-initiated polymerization of dimethylsulfoxonium methylic and constitutes a powerful tool for the synthesis of well-defined perfectly linear polymethylene (equivalent to PE).\textsuperscript{18-20} The general mechanism involves the formation of an organoboron complex between the ylide (monomer) and the organoborane (initiator), through an attack of the nucleophilic monomer to the Lewis acidic initiator. This is followed by migration/insertion of –CH\textsubscript{2}– moiety into the three alkyl branches of the initiator with the simultaneous release of dimethyl sulfoxide. As a result, the methylene groups are inserted one by one (C1 polymerization) into the initiator, leading to a 3-arm PE star with boron at the junction point. The final step involves oxidation/hydrolysis of the 3-arm star PE to afford hydroxyl-terminated linear PE (PE-OH). This strategy, in combination with other polymerization methods, was employed for the synthesis of a plethora of PE-based architectures. For example, the PE-OH has been used as a macroinitiator for ROP,\textsuperscript{21} and after transformation for ATRP\textsuperscript{22-24} or reversible-addition fragmentation chain-transfer polymerization (RAFT)\textsuperscript{25} to generate different PE-based
block copolymers. Moreover, graft (comb) (co)polymers or molecular brushes were synthesized by reaction of PE-OH with functionalized monomers to generate macromonomers, followed by (co)polymerization.\textsuperscript{26}

Our group has developed this perfect polymerization method to synthesize a variety of PE-based materials, including linear and complex macromolecular architectures, such as stars and cyclic homo/copolymers, also employing new borane initiators and different functionalized ylides.\textsuperscript{27,35} Particularly in the case of miktoarm PE-based stars, to the best of our knowledge, only a few examples exist in the literature, and these are given below. 3-Miktoarm stars of PE-PS\textsubscript{2} and PE-PMMA\textsubscript{2} have been synthesized via the combination of polyhomologation and ATRP.\textsuperscript{36} We have also reported the synthesis of PE-based 3-miktoarm stars of PE\textsubscript{2}-PS, based on polyhomologation initiated by B-thexylsilaboracyclic derivatives, bearing two silicon-connected initiating sites with one site blocked, and ATRP.\textsuperscript{37} Additionally, using a novel multi-heterofunctional initiator, PE-based 3-miktoarm star copolymers PE\textsubscript{2}PS, (PE-\textit{b}-PS)\textsubscript{2}PS and terpolymers (PE-\textit{b}-PMMA)\textsubscript{2}(PS-\textit{b}-PMMA) were synthesized by combining boron chemistry, polyhomologation and ATRP.\textsuperscript{38}

Recently, we reported a one-pot methodology for the synthesis of perfectly linear \(\omega\)-hydroxyl PE-based block copolymers (PS-\textit{b}-PE-OH and PBd-\textit{b}-PE-OH) combining anionic polymerization and polyhomologation, through a linking agent (BF\textsubscript{3}OEt\textsubscript{2}).\textsuperscript{39} Furthermore, we developed this strategy for the synthesis of PE-based star-block copolymers (PS-\textit{b}-PE)\textsubscript{3}C-OH and (PI-\textit{b}-PE)\textsubscript{3}C-OH, where PI: polyisoprene, via a transformation of the air-sensitive boron junction point of 3-arm star PE to stable carbon-linked 3-arm star PE by using “stitching” reaction.\textsuperscript{40} In the present work, we expand this methodology to the synthesis of well-defined complex miktoarm star co/terpolymers, consisting of polyisoprene (PI), polystyrene (PS) and polyethylene (PE), combining anionic polymerization high vacuum techniques and polyhomologation. DSC shows a clear glass transition (\(T_g\)) of the PI component in all samples and the melting behavior of the crystalline PE block. Simultaneous SAXS and WAXS as a function of sample temperature showed the appearance of periodic microphase separation and PE block crystallization in several samples. TEM of microtomed, stained samples allowed direct imaging of the self-assembled microdomain morphology in several samples.
EXPERIMENTAL SECTION

Materials. Benzene (Sigma-Aldrich, 99%), toluene (VWR Chemicals, 99%), hexane (VWR Chemicals, 99%) and trichloromethylsilane (Sigma-Aldrich, 99%) were purified by high-vacuum techniques (HVT) and standard procedures, based on the requirements of anionic polymerization, described in details elsewhere.\textsuperscript{41,42} Styrene (Sigma Aldrich, 99%) was purified by distillation over CaH\textsubscript{2} and subsequently over di-\textit{n}-butylmagnesium (Sigma-Aldrich, 1 M solution in heptane) and stored at -20 °C in pre-calibrated ampoules. Isoprene (Sigma Aldrich, 99%) was purified over CaH\textsubscript{2}, distilled twice over \textit{n}-BuLi, remained under stirring for 30 min at 0 °C and finally stored at -20 °C in pre-calibrated ampoules. 1,3-Butadiene (Sigma-Aldrich, 99%) was purified \textit{via} sequential distillations over \textit{n}-BuLi at -10 °C using ice/salt bath, prior addition to the polymerization reactor. Boron trifluoride diethyl etherate (BF\textsubscript{3}OEt\textsubscript{2}) (Fluka) was distilled over CaH\textsubscript{2} and diluted in benzene before use.

Methyltriphenylphosphonium iodide (Sigma-Aldrich, 97%), \textit{n}-butyllithium (1.6 M in hexane, Sigma-Aldrich), \textit{sec}-butyllithium (1.4 M in cyclohexane, Sigma-Aldrich), 4-bromobenzophenone (Sigma-Aldrich, 98%), 1,2-dibromoethane (Acros Organics, 99%) and MgSO\textsubscript{4} were used as received. Magnesium turnings (Sigma-Aldrich) were activated through sequential washings with 0.1 N HCl solution, distilled water and acetone and dried under vacuum until constant weight.

Trimethylsulfoxonium iodide (Sigma-Aldrich, 98%), benzyltributylammonium chloride (Sigma-Aldrich, 98%), and trimethylamine-\textit{N}-oxide dehydrate (TAO-2H\textsubscript{2}O) (>99%, Fluka) were used as received. Tetrahydrofuran (THF) (Sigma-Aldrich, 99.9%) was refluxed over sodium, stirred in the presence of CaH\textsubscript{2} overnight and distilled over Na/K alloy. Sodium hydride (60% dispersion in mineral oil, Sigma-Aldrich) was washed with petroleum ether or hexane (40-50 °C) before use. Celite 545\textsuperscript{(R)} (Sigma-Aldrich) was dried at 150 °C for 48 h before use. Dimethylsulfoxonium methyldide was prepared according to Corey’s method followed by the switch of the solvent from THF to toluene.\textsuperscript{43}

Instrumentation. Size exclusion chromatography measurements were carried out at 35 °C through a Viscotek GPCmax VE-2001 with THF as the eluent at a flow rate of 1.0 mL/min, equipped with an isocratic pump, Styragel HR2 and HR4 columns in series (300 mm × 8 mm) and a differential refractive index.
detector (DRI). The system was calibrated with polystyrene (PS) standards (Mp: 370 to 4,220,000 g/mol) (PDI).

Triple-detection measurements were performed in the same instrument, which was also equipped with a two-angle light scattering detector (15° and 90°, λ = 658 nm) and a viscometer. These measurements were used for the calculation of the weight-average molecular weight (Mw) and polydispersity index (Ð) of the linear and living star precursors. In the case of PE-based copolymers and terpolymers, high temperature size exclusion chromatography (HT-SEC) measurements were conducted in a Viscotek HT-GPC Module 350 at 150 °C with 1,2,4-trichlorobenzene (TCB) as the eluent solvent (1 mL/min), equipped with two PLgel 10 μm MIXED-B columns, a refractive index detector, a light scattering detector (λ = 670 nm) and a viscometry detector. Triple-detection HT-SEC measurements were also carried out in the same instrument in order to calculate the weight-average molecular weight (Mw) and the polydispersity of the final miktoarm star copolymers and terpolymers. Proton and carbon nuclear magnetic resonance spectroscopy (1H-NMR and 13C-NMR) spectra were recorded at Bruker AVANCE III spectrometers operating at 500 or 600 MHz. Chloroform-d (CDCl3) was used as the solvent for the initial star precursors (500 MHz) at room temperature (r.t), while toluene-d₈ for the final PE-based star polymers, at 80 °C. Differential scanning calorimetry (DSC) measurements were performed on a Mettler Toledo DSC1/TC 100 system. The samples were heated from room temperature to 150 °C in order to erase the thermal/solvent history, cooled to -100 °C and heated again to 150 °C, with a heating/cooling rate of 10 °C/min. This cycle was repeated several times until constant glass transition temperatures (Tg) and Tm were recorded. Moreover, the degree of crystallinity of the PE component was calculated through the equation: 

\[ X_c = \Delta H_m f_{PE} / \Delta H_m^* \]

where \( f_{PE} \) is the weight fraction of PE block and \( \Delta H_m (288 \text{ kJ kg}^{-1}) \) is the specific enthalpy of melting for 100% crystalline PE.⁴⁴

Direct morphological observation of the microdomain structures of the 3-arm star copolymers and terpolymer was performed by TEM using two different instruments: a FEI Tecnai Electron Microscope operated at 120 kV, and a JEOL 1230 TEM operated at 80 kV. Prior to X-ray and microtome/TEM characterization, samples were processed to promote periodic organization of the microdomains and PE crystallinity. Samples are prepared by using either a solvent crystallization route, followed by annealing or by heating into the melt state above both the order-disorder transition (ODT) and the melting transition (Tm).
followed by cooling below the ODT or crystallization temperature \((T_c)\). The solvent route first dissolves the polymer at high temperature in a xylene solution followed by cooling to an intermediate temperature to induce PE crystallization, followed by cooling and drying and then annealing below the \(T_m\) of the PE component. The melt processing route takes a dry, previously solvent cast sample, to a temperature above both the ODT and \(T_m\) into the homogeneous melt state, followed by cooling to a temperature below \(T_m\) and isothermally holding to allow crystallization of the PE component. The \(\text{PL}_2(\text{PS}-b-\text{PE})\)-OH sample was annealed just below the PE melting point at 110 °C for 24h. The \(\text{PL}_2(\text{PI}'-b-\text{PE})\)-OH sample was first dissolved in xylene at 87 °C and then slowly cooled over 60 minutes to 50 °C and the solution then kept at 50 °C for 5 days, before cooling to room temperature and the xylene allowed to slowly evaporate (~ 6 days to dryness). The solution-processed \(\text{PL}_2-(\text{PI}'-b-\text{PE})\)-OH was then employed for \textit{in-situ} simultaneous SAXS and WAXS heating experiments. During the thermal \textit{in-situ} X-ray experiments, the sample was heated to a series of targeted temperatures and kept at each temperature for 20 min before X-ray characterization. Subsequent to the SAXS and WAXS, the samples were further examined by TEM after microtomy and staining. A Leica EM UC7 ultra-cryomicrotome with a diamond knife was used to cut 50-60 nm thick sections at cryogenic conditions (-120 °C). Sections were picked up onto copper grids and in order to increase the contrast for TEM observation, stained with osmium tetroxide (OsO₄) for 1 h for \(\text{PL}_2(\text{PI}'-b-\text{PE})\)-OH and for 16h for the \(\text{PL}_2(\text{PS}-b-\text{PE})\)-OH star terpolymer.

X-ray experiments were performed using synchrotron X-ray and lab X-ray: the 12-ID-B synchrotron station at the Advanced Photon Source of Argonne National Laboratory with X-ray energy of 14 KeV \((\lambda = 0.089 \text{ nm})\) is equipped with a SAXS detector (Pilatus 2M) and a WAXS detector (Pilatus 300K). We also made room temperature SAXS measurements using a Rigaku S-Max 3000 SAXS instrument (Cu K\(\alpha\) radiation, \(\lambda =0.154 \text{ nm}\)) at the University of Houston. The X-ray patterns are presented in the form of intensity \((I)\) versus scattering vector magnitude \(|\vec{q}| = q = 4\pi\lambda^{-1}\sin(\frac{\theta}{2})\), where \(\theta\) is the scattering angle and \(\lambda\) is the radiation wavelength.
Synthesis of 4-(Dichloromethylsilyl)diphenylethylene. Initially, 4-bromodiphenylethylene was obtained from the Wittig reaction of 4-bromobenzophenone and methyltriphenylphosphonium iodide in the presence of n-BuLi and THF. Subsequently, 4-(dichloromethylsilyl)diphenylethylene (DCMSDPE) was prepared from the Grignard reagent of 4-bromodiphenylethylene and excess of trichloromethylsilane, using high vacuum techniques and custom-made glass apparatuses. Finally, DCMSDPE was distilled into pre-calibrated ampules (at ~110 °C), diluted in benzene and stored at -20 °C. The ¹H- and ¹³C-NMR spectra (Figures S1 and S2) confirmed the successful synthesis of DCMSDPE. More details for the synthetic procedure are given in a previous paper.⁴⁵

Synthesis of 3-arm “Living” Stars. All synthetic procedures were conducted with conventional high-vacuum techniques. The anionic polymerization and linking reactions were carried out in evacuated, n-BuLi washed custom-made glass reactors, at room temperature. Reagents were added via break-seals and aliquots for characterization were taken by heat-sealing of constrictions at all steps. More details concerning the techniques and the apparatuses used are given to previous reports.⁴¹,⁴² As an example, the synthesis of the (PI₂)PI’ 3-arm homopolymer “living” star is given below.

Initially, the PI⁺ was obtained by anionic polymerization of isoprene (6 g, 88.23 mmol) with sec-BuLi (0.67 mmol) in benzene at room temperature for 24 h. The living homopolymer was collected in a pre-calibrated flask equipped with break-seal and connected to another apparatus. The PI⁺ (ₚ = 9.2 kg/mol, 0.67 mmol) was added dropwise to the reactor containing DCMSDPE (0.22 mmol) in benzene (50 mL) under vigorous stirring. The reaction was monitored by taking aliquots frequently and analyze them by SEC. After the addition of two equivalents of PI⁺ (0.44 mmol), with regard to DCMSDPE, and the end point was also confirmed by SEC, the titration was stopped. The flask containing the solution of the in-chain double bond intermediate product was attached to a new apparatus, where the appropriate amount of sec-BuLi (0.22 mmol) was added. The color of the solution turned to dark red, indicating the reaction of sec-BuLi with the double bond of the diphenylethylene moiety. The solution was left under stirring for 48 h to ensure that all DPE groups reacted with the initiator (sec-BuLi). Subsequently, a new amount of isoprene (5.2 g, 76.4 mmol) was added, and after complete polymerization (24 h) an aliquot was removed
from the reactor for SEC measurements. Finally, the solution was transferred to a flask equipped with a break-seal. Triple-detection SEC measurements were carried out in THF (35 °C) for calculation of the molecular characteristics of the initial PI arm and the 3-arm PI star ($M_w^{PI} = 9.2$ kg/mol, $D = M_w/M_n = 1.03$, $M_w^{star} = 44.1$ kg/mol, $D = 1.04$). The same procedure was followed for the synthesis of the other two “living” stars reported in this work. In the case of PI2PS-Li“, styrene monomer was added in the anionic site generated from the reaction of the in-chain double bond with sec-BuLi (Scheme S1), while in the living PI double-tailed (PI2dtDPE-Li+) sample, oligomerization of a few 1,3-Bd monomeric units (4-6) was carried out (Scheme S2). As previously reported, triple-detection SEC measurements along with $^1$H-NMR experiments (in the case of PI2PS star copolymer, Figure S3) were conducted for the calculation of the molecular characteristics in each case (for PI2PS: $M_w^{PI} = 9.3$ kg/mol, $D = 1.03$, $M_w^{star} = 27.8$ kg/mol, $D = 1.05$ and for PI2Bd end-capped: $M_w^{PI} = 11.3$ kg/mol, $D = 1.03$, $M_w^{star} = 22.4$ kg/mol, $D = 1.04$).

**Synthesis of Tricicromolecular Borane Initiators [(PI2PI)3B, (PI2PS)3B and (PI2)3B] for Polyhomologation.** In a typical experiment, a flask containing the PI2PI´Li+ star and an ampoule of diluted BF3OEt2 solution in benzene, were attached to a custom-made glass apparatus. High vacuum techniques were also employed in this case. The linking reaction of the “living” star with BF3OEt2 was carried out in evacuated, n-BuLi washed reactor at r.t. Initially 0.12 mmol of PI2PI´Li+ were inserted in the reactor containing also 50 mL of purified benzene solvent. Subsequently, 0.033 mmol of BF3OEt2 was slowly added and stirred for 4 days at r.t. (protected from intense light) to afford the macroinitiator [(PI2PI)3B]. Upon following the same method, 3-arm boron-linked stars of (PI2PS)3B and (PI2)3B type were also synthesized.

**Polyhomologation of dimethylsulfoxonium methylide by macro-boron macroinitiators.** A typical procedure is as follows. In the reactor used for the synthesis of the macro-boron initiator (PI2PI´)3B, 80 mL of dimethylsulfoxonium methylide solution in toluene (0.8 M) was added and the mixture heated to 70 °C and left under stirring for 2 h to afford [PI2(PI´-b-PE)]3B. Afterwards, TAO2H2O (0.16 mmol) was added and the oxidation/hydrolysis left to proceed at 70 °C for 12 h. Then, the solution was poured into large excess of cold methanol to precipitate the polymer. The resultant star copolymer [PI2(PI´-b-PE)-OH] was
collected after fractionation by centrifugation in toluene at -5 °C and dried under vacuum for at least 24 h. The fractionation was carried out several times, until there was not any (PI)₂(PI)’ residual left in the HT-SEC traces. Following the same procedure, (PI)₂(PS-b-PE)-OH (Scheme S3) and (PI)₂(PE)-OH (Scheme S4) miktoarm star polymers were also synthesized.

RESULTS AND DISCUSSION

Synthesis of “Living” Stars. The key molecule in the synthesis of a “living” star is 4-(dichloromethylsilyl)diphenylethylene (DCMSDPE) linking agent, which bears two chlorosilane groups (SiCl₂) and one non-homopolymerizable double bond. The general reactions followed for the synthesis of DCMSDPE are presented in Scheme 1.

Scheme 1. General reactions for the synthesis of 4-(dichloromethylsilyl)diphenylethylene.

The synthesis of a 3-arm “living star” is based on the selective reaction of polyisoprenyl lithium (PI-Li⁺) with the two chlorines of DCMSDPE by careful titration, the addition of sec-BuLi to the in-chain double bond of the intermediate product and finally the polymerization of a new monomer from the created anionic site to generate the third arm. The methodology given in the experimental section led to the synthesis of three different “living” stars [(PI)₂(PI)’Li⁺, (PI)₂(PS)Li⁺ and (PI)₂(Bd)Li⁺]. The general synthetic route followed is presented in Scheme 2, which refers to the synthesis of (PI)₂(PI)’Li⁺.
The initial step of the synthesis involved the titration of the two chlorine atoms of DCMSDPE with anionically prepared PI-Li+. When DCMSDPE is allowed to react with nucleophilic living chains, the reaction with the chlorosilane groups is faster than the addition to the double bond, due to steric hindrance of the two phenyl groups of the DPE.\textsuperscript{46,47}

**Scheme 2.** General reactions for the synthesis of 3-arm \((\text{PI})_2\text{PI}^\text{'}\) “living” star.

![Scheme 2 diagram](image)

**Table 1.** Molecular characteristics of “living” stars.

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<th>Sample</th>
<th>(^{a}M_w^{PI}) (kg/mol)</th>
<th>(^{a}D_{PI})</th>
<th>(^{a}M_w^{star}) (kg/mol)</th>
<th>(^{a}D_{star})</th>
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<td>((\text{PI})_2\text{PI}^\text{'})</td>
<td>9.2</td>
<td>1.03</td>
<td>44.1</td>
<td>1.04</td>
</tr>
<tr>
<td>((\text{PI})_2\text{PS})</td>
<td>9.3</td>
<td>1.03</td>
<td>27.8\textsuperscript{b}</td>
<td>1.05</td>
</tr>
<tr>
<td>((\text{PI})_2\text{Bd end-capped})</td>
<td>11.3</td>
<td>1.03</td>
<td>22.4</td>
<td>1.04</td>
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\(^{a}M_w\) was determined by triple-detection SEC in THF at 35 °C. The dn/dc value of PI that used was 0.130 mL/g. \(^{b}\) dn/dc value of the miktoarm star copolymer was calculated to be 0.148 mL/g, by using the weight fractions of PS and PI obtained from \(^{1}\text{H}\)-NMR measurements in CDCl\(_3\), assuming the dn/dc value of PI 0.130 mL/g and of PS 0.185 mL/g.

Concerning the synthesis of the \((\text{PI})_2\text{PI}^\text{'}\text{Li}^+\) living star (Table 1), the solution of PI living chains in benzene (5% w/v) was slowly added dropwise (titration) to the reactor containing DCMSDPE in benzene under vigorous stirring. In this way, local excess of the living chains is avoided, and the chlorines are substituted one by one. Although both chlorines are initially equal in reactivity, after the replacement of the
first chlorine, the reactivity of the second one is much lower due to the steric hindrance imposed by the already incorporated first chain. In the beginning of the titration, a relatively fast rate of addition was feasible, but as the titration continued, the rate of addition was decreased in order to control the stoichiometry. The addition was carried out over a period of 48 h and a permanent pale yellow color appeared, due to the reaction with the double bond of DCMSDPE, showing the end point of the titration.

The progress of the linking reaction was monitored by removing aliquots from the reactor and analyzing them by SEC (Figure 1a-d). Initially, there is only one peak on the SEC chromatograph, attributing to the end double-bond PI with one chlorine (Figure 1b). As the titration proceeds, this peak decreases while that of the PI double-tailed DPE (PI₂dtDPE) increases (Figure 1c). The disappearance of the peak corresponding to (I) indicates the end of the titration (Figure 1d).

The reaction of sec-BuLi with the double bond of dtDPE was confirmed by the instantaneous change of the solution color from pale yellow to deep red, an indication for the formation of DPE·Li⁺. As it was mentioned before, it is very important to control the stoichiometry, otherwise the byproducts formed would complicate the synthesis since they are not isolated (one-pot procedure). Subsequently, new amount of isoprene was added and the polymerization allowed to proceed for 24 h, leading to the 3-arm (PI₂PI’ living star (Figure 1, e). The target molecular weight of the new PI branch was estimated from the moles of DPE·Li⁺ and the quantity (g) of the monomer and its actual molecular weight was calculated indirectly from the triple-detection SEC measurements of the 3-arm star, since the branch could not be isolated ($M_w^{PT} = 25.7$ kg/mol).
The same synthetic procedure, as described above, was also followed in the cases of the (PI)$_2$PS Li$^+$ and (PI)$_2$Bd end-capped living stars. In the first one (Table 1), styrene monomer was added to PI$_3$dtDPE$^-$ Li$^+$ and left for polymerization (24 h) (Scheme S1) while in the second one (Table 1), a few monomeric units of 1,3-butadiene, respectively (Scheme S2). The progress of the linking reactions and the polymerization of the new monomers was also monitored through SEC measurements in both cases (Figure 2). $^1$H-NMR measurements were carried out for (PI)$_2$PS star copolymer to determine the weight fraction of each block ($f_{PI} = 0.67$ and $f_{PS} = 0.33$) (Figure S3). The narrow molecular weight distribution obtained by SEC and confirmed by triple-detection SEC measurements, as well as the agreement between the calculated and experimental values of $M_n$ for all samples indicate a high degree of molecular and structural homogeneity. The molecular characteristics of the precursors (linear PI) and the final living stars are demonstrated in Table 1.

**Figure 1.** SEC (THF, 35 °C, DRI detector) traces of: a) “Living” linear PI, b) monosubstituted DCMSDPE, c) intermediate product after the substitution of one chlorine during the linking reaction, d) PI$_2$dtDPE and e) final 3-arm (PI)$_2$PI$^-$ living star.
Synthesis of Boron-linked Macroinitiators and Polyhomologation of Dimethylsulfoxonium Methylide. The macro-boron initiators were prepared through the linking reaction of living star precursors (20% excess) with BF$_3$OEt$_2$, generating boron-linked dendrimer-like intermediate products and used without isolation for the polyhomologation of dimethylsulfoxonium methylide (Scheme 3). An excess of the living star precursor was required to drive the reaction to completion, as in the case of chlorosilane linking chemistry.$^4$ The yield of this reaction is almost 100%. Due to the high sensitivity of boranes to air (oxygen and moisture), it was not feasible to analyze the dendrimer-like macroinitiators formed by SEC since the borane species decompose during analysis. This decomposition was confirmed in a recent report after the linking reaction of living macroanions with BF$_3$OEt$_2$, by taking aliquots at different time intervals and characterize them via SEC.$^{40}$

**Scheme 3.** Synthetic route followed for the synthesis of miktoarm star copolymer PI$_2$(PI’-b-PE)-OH.
Trimacromolecular boranes [(PI<sub>2</sub>PI<sub>′</sub>)<sub>3</sub>B, (PI<sub>2</sub>PS)<sub>3</sub>B and (PI<sub>2</sub>Bd end-capped)<sub>3</sub>B] were directly used as initiators for the in situ “living” polyhomologation of dimethylsulfoxonium methylide in toluene at 70-80 °C, resulting to the corresponding boron-linked dendrimer-like [PI<sub>2</sub>PI<sub>′</sub>-b-PE]<sub>3</sub>B, [PI<sub>2</sub>PS-b-PE]<sub>3</sub>B and [(PI<sub>2</sub>)PE]<sub>3</sub>B co/terpolymers. Oxidation/hydrolysis of these co/terpolymers with trimethylamine N-oxide dehydrate (TAO) led to the final miktoarm star co/terpolymers [PI<sub>2</sub>(PI<sub>′</sub>-b-PE)-OH, PI<sub>2</sub>(PS-b-PE)-OH and (PI<sub>2</sub>)PE-OH], bearing an –OH group at PE chain-end. After polyhomologation and cooling at room temperature the toluene solution turned cloudy, thus indicating the successful formation of the polyethylene block in all cases. A purification step was necessary for all samples, to eliminate the excess (purposely added) of the corresponding living star precursor. The molecular characteristics of the linear, living star precursors, along with the final miktoarm star polymers are presented in Table 2.

**Table 2. Molecular characteristics of PE-based miktoarm star co/terpolymers.**

<table>
<thead>
<tr>
<th>Sample</th>
<th>&lt;sup&gt;a&lt;/sup&gt;&lt;i&gt;M&lt;sub&gt;n&lt;/sub&gt;&lt;/i&gt;&lt;sup&gt;living star&lt;/sup&gt; (kg/mol)</th>
<th>&lt;sup&gt;a&lt;/sup&gt;&lt;i&gt;M&lt;sub&gt;n&lt;/sub&gt;&lt;/i&gt;&lt;sup&gt;living star&lt;/sup&gt; (kg/mol)</th>
<th>&lt;sup&gt;a&lt;/sup&gt;&lt;i&gt;M&lt;sub&gt;n&lt;/sub&gt;&lt;/i&gt;&lt;sup&gt;final star&lt;/sup&gt; (kg/mol)</th>
<th>&lt;sup&gt;a&lt;/sup&gt;&lt;i&gt;D&lt;sub&gt;n&lt;/sub&gt;&lt;/i&gt; (%)</th>
<th>&lt;sup&gt;d&lt;/sup&gt;&lt;i&gt;f&lt;sub&gt;PI&lt;/sub&gt;&lt;/i&gt; (%)</th>
<th>&lt;sup&gt;d&lt;/sup&gt;&lt;i&gt;f&lt;sub&gt;PS&lt;/sub&gt;&lt;/i&gt; (%)</th>
<th>&lt;sup&gt;d&lt;/sup&gt;&lt;i&gt;f&lt;sub&gt;PE&lt;/sub&gt;&lt;/i&gt; (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>(PI&lt;sub&gt;2&lt;/sub&gt;)PE-OH</td>
<td>11.3</td>
<td>22.4</td>
<td>6.8</td>
<td>30.3</td>
<td>1.12</td>
<td>75</td>
<td>-</td>
</tr>
<tr>
<td>PI&lt;sub&gt;2&lt;/sub&gt;(PI&lt;sub&gt;′&lt;/sub&gt;-b-PE)-OH</td>
<td>9.2</td>
<td>44.1</td>
<td>7.9</td>
<td>56.4</td>
<td>1.14</td>
<td>79</td>
<td>-</td>
</tr>
<tr>
<td>PI&lt;sub&gt;2&lt;/sub&gt;(PS-b-PE)-OH</td>
<td>9.3</td>
<td>27.8</td>
<td>8.3</td>
<td>38.4</td>
<td>1.13</td>
<td>50</td>
<td>22</td>
</tr>
</tbody>
</table>

<sup>a</sup><i>M<sub>n</sub></i><sup>living star</sup> was determined by triple-detection SEC in THF at 35 °C. <sup>b</sup><i>M<sub>n</sub></i><sup>PI</sup> was calculated from <sup>1</sup>H-NMR spectra using the area ratio of protons in terminal –CH<sub>2</sub>OH at δ = ~3.4-3.5 ppm to the ones on the backbone. <sup>c</sup><i>M<sub>n</sub></i><sup>final star</sup> and <i>D</i> = <i>M<sub>n</sub></i>/<i>M<sub>n</sub></i> were determined by triple-detection HT-SEC in 1,2,4-trichlorobenzene at 150 °C. <sup>d</sup>volume fraction of PI block, PS block and PE block; the calculation is based on <i>M<sub>n</sub></i> measured by SEC.
Specifically, the synthesis of PI₂(PI’-b-PE)-OH was monitored by HT-SEC measurements (Table 2) in 1,2,4-trichlorobenzene (TCB) at 150 °C calibrated with PS standards (Figure 3). It is evident that the peak appearing after the polyhomologation (Figure 3b) shifts to higher molecular weights (lower elution volumes), whereas the second peak in the lower molecular weight region corresponds to the excess of the living star precursor. To eliminate this peak, the mixture after the polyhomologation was dissolved in toluene at high temperature (80 °C) to give a clear and transparent solution, followed by cooling to room temperature and finally centrifuged at low temperature (-5 °C). This procedure was repeated several times until the HT-SEC trace showed the complete elimination of the living star precursor (Figure 3c). Finally, the weight-average molecular weight and the polydispersity index were calculated by triple-detection HT-SEC measurements ($M_w = 56.4$ kg/mol and $D = 1.14$).

As shown in Figure 4, $^1$H-NMR measurements in toluene-$d_8$ at 80 °C revealed the characteristic chemical shift of PE at $\delta = 1.4$ ppm (-CH$_2$-), the chemical shift of the –CH$_2$- protons connected to the hydroxyl group (-CH$_2$-OH) at $\delta = 3.6$ ppm and the signal assigned to the protons of the PI arms appears at $\delta = 4.8$-5.4 ppm. The weight fractions of each block (PI and PE) and the degree of polymerization for the PE component ($f_{PI} = 0.82$, $f_{PE} = 0.18$ and $DP_{PE} = 282$) were calculated, by end-group analysis. Moreover, the PI arms of the miktoarm star copolymer were synthesized via anionic polymerization in hydrocarbon solvent (benzene); thus, it is obvious the high 1,4-microstructure (~ 90%).
Figure 3. HT-SEC traces of a) (PI)₂PI’ 3-arm living star precursor, b) PI₂(PI’-b-PE)-OH miktoarm star copolymer after polyhomologation (unfractionated) and c) final PI₂(PI’-b-PE)-OH miktoarm star copolymer after fractionation.

Figure 4. ¹H-NMR (600 MHz) of PI₂(PI’-b-PE)-OH miktoarm star copolymer in toluene-d₈ (80°C).

The synthetic procedure that followed in the case of PI₂(PS-b-PE)-OH (Table 2) miktoarm star terpolymer was similar to the one described above (Scheme S3). An excess (20%) of the PI₂PS living star precursor was used for the linking reaction with BF₃OEt₂, forming the borane macroinitiator for the in situ
polyhomologation of dimethylsulfoxonium methyldide in toluene at 80 °C. HT-SEC measurements were conducted for monitoring the synthesis of the miktoarm star terpolymer (Figure 5). It is clear that the peak appearing after the polyhomologation (Figure 5b) moves to higher molecular weights compared to the HT-SEC trace of the living star precursor (Figure 5a). The second peak in the lower molecular weight region is attributed to the excess of the living star precursor that didn’t react with the linking agent. The purification step (centrifugation) described above was also followed in this case for the elimination of the living star precursor (Figure 5c). The weight-average molecular weight and the polydispersity index were calculated by triple-detection HT-SEC measurements ($M_w = 38.4$ kg/mol and $D = 1.13$), indicating a high degree of molecular and structural homogeneity.

![Figure 5. HT-SEC traces of a) (PI)$_2$PS 3-arm living star precursor, b) PI$_2$(PS-b-PE)-OH miktoarm star terpolymer after polyhomologation (unfractionated) and c) final PI$_2$(PS-b-PE)-OH miktoarm star terpolymer after fractionation.](image)

Additional evidence for the successful synthesis of PI$_2$(PS-b-PE)-OH miktoarm star terpolymer was derived from $^1$H-NMR results. According to a previous report, the methylide monomer cannot be polymerized either by the macroanion or by BF$_3$:OEt$_2$. This proves that only the boron-linked 3-arm star polymer has the ability for polyhomologation. As shown in Figure S4, the characteristic chemical shift of PE appears at $\delta = 1.4$ ppm (–CH$_2$–), the chemical shift of the –CH$_2$– protons connected to the hydroxyl group.
(-CH₂-OH) at δ = 3.4 ppm and the signals assigned to the protons of the PI arms and to aromatic protons of the PS block appear at δ = 4.8-5.4 ppm and at δ = 6.5-6.9 ppm respectively. By end-group analysis, the weight fraction of each block (fᵢ = 0.53, fᵢₛ = 0.27 and fᵢₑ = 0.20) and the degree of polymerization of PE component (DPₑ = 296) were calculated.

The final miktoarm star copolymer synthesized in this work was (PI)₂PE-OH (Table 2), following the same synthetic route as previously mentioned (Scheme S4). In this case, after the synthesis of the PI₃dtDPE⁻Li⁺, a few monomeric units of 1,3-Bd were introduced, to change the nature of active species to polybutadienyl lithium (PBD⁻Li⁺). In this way, the steric hindrance caused by the diphenyl groups of DPE was reduced, and the linking reaction with BF₃OEt₂ was facilitated. The successful polyhomologation of dimethylsulfoxonium methyldiene from the boron-linked macroinitiator was confirmed by HT-SEC and ¹H-NMR results.

After the polyhomologation of dimethylsulfoxonium methyldiene, the HT-SEC trace revealed a peak at higher molecular weight compared to the living star precursor, also having a second peak (at higher elution volumes) corresponding to the excess of the living star precursor (Figure 6b). After centrifugation in toluene at low temperature (-5 °C), the elimination of the second peak was succeeded, and a clear peak was obtained (Figure 6c). The molecular characteristics were determined through triple-detection HT-SEC measurements (Mₛ = 30.3 kg/mol and D = 1.12) and ¹H-NMR measurements. The ¹H-NMR spectrum in Figure S5 revealed the PE fingerprint with the characteristic chemical shift at δ = 1.4 ppm (-CH₂-), the PI fingerprint at δ = 4.8-5.4 ppm and the chemical shift of the -CH₂- protons connected to the hydroxyl group (-CH₂-OH) at δ = 3.5 ppm. The weight fraction of each block and the degree of polymerization of PE component were calculated by end-group analysis (fᵢ = 0.77, fᵢₑ = 0.23 and DPₑ = 243).
Figure 6. HT-SEC traces of a) (PI)$_2$Bd end-capped living star precursor, b) (PI)$_2$PE-OH miktoarm star copolymer after polyhomologation (unfractionated) and c) final (PI)$_2$PE-OH miktoarm star copolymer after fractionation.

The comparison between the unfractionated HT-SEC chromatographs of all 3-miktoarm star co/terpolymers after the polyhomologation (Figure 3b, 5b and 6b) showed that the linking reaction of PI$_2$PI’ living star with BF$_3$OEt$_2$ was more efficient than in the case of PI$_2$PS, due to the rigid nature of PS compared to the soft and flexible PI. The steric hindrance effect of PI$_2$dtDPELi$^+$, even though it was end-capped with 4-6 monomeric units of 1,3-Bd, was still higher than the other cases.

**DSC Analysis of PE-based Star Co/Terpolymers.** A set of samples were heated from 20 °C to 150 °C to erase their prior solvent and thermal history, then cooled to -100 °C and heated again to 150 °C, with a heating/cooling rate of 10 °C/min (see thermal traces in Figure 7). Under these rapid cooling conditions, upon heating, the PI$_2$(PI’-$b$-PE)-OH star copolymer exhibits a $T_m$ of 112 °C for the PE domains while the $T_g$ of the PI is -58 °C. Similar results were also obtained for the PI$_2$(PS-$b$-PE)-OH star terpolymer ($T_m$ at 113 °C and $T_g$ at -58 °C) with the $T_g$ of the PS segment obscured by the onset of the melting of the PE. The thermal trace of the (PI)$_2$PE-OH star copolymer showed a slightly lower $T_m$ at 108 °C and $T_g$ at -60 °C. The crystallinity of the PE component in the three stars varied from 57.2% to 56.5 % to 51.5%, respectively.
The lower melting temperature and crystallinity of the PE component in the (PI)$_2$PE-OH star copolymer, compared to the other two miktoarm stars can be ascribed to the lower chain length of PE.

Figure 7. DSC traces for PI$_2$(PI’-b-PE)-OH, PI$_2$(PS-b-PE)-OH and (PI)$_2$PE-OH.

Morphological Characterization. The different components have a wide variation in their mutual compatibility. In Table 3, we use the square of the Hildebrand solubility parameters difference for each pair of components and their respective degrees of polymerization to estimate a degree of segregation for each pair of components. The degree of segregation varies by nearly a factor of 50X from the low value for PI-PE to the high values of both PI-PS and PE-PS.

<table>
<thead>
<tr>
<th>Sample</th>
<th>Degree of segregation (PI-PE pair) (MPa)</th>
<th>Degree of segregation (PI-PS pair) (MPa)</th>
<th>Degree of segregation (PE-PS pair) (MPa)</th>
</tr>
</thead>
<tbody>
<tr>
<td>(PI)$_2$PE-OH</td>
<td>26.2</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>PI$_2$(PI’-b-PE)-OH</td>
<td>46.9</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>PI$_2$(PS-b-PE)-OH</td>
<td>27.5</td>
<td>1288.7</td>
<td>1193.7</td>
</tr>
</tbody>
</table>

The degree of segregation is calculated based on $(N_A + N_B) \times \Delta \delta^2$, where $N_A$ and $N_B$ are the number of repeated unit in block A and block B, respectively, and $\Delta \delta$ is the solubility parameter difference between block A and block B. The calculations are based on $M_w$ measured by SEC.
The weakly segregated (PI₂)-PE-OH and PI₂(PI’-b-PE)-OH star samples while showing crystallinity in the PE block from the DSC (and WAXS vide infra) results do not exhibit any periodic domain ordering in SAXS or in TEM. The (PI₂)-PE-OH SAXS scattering curve shows a strong monotonic decrease in the I(q) with angle, while the PI₂(PI’-b-PE)-OH shows a weak, broad shoulder, corresponding to a spacing of ~17 nm (arrow). The weak scattering in these samples is due to the relatively small electron density differences between PI and PE (305.6 e/nm³ for PI (density 0.91 g/cm³), and 343.4 e/nm³ for PE (density 1 g/cm³)) and the lack of any long-range order of the PE crystals.

**Figure 8.** (a) SAXS curves for samples (PI₂)-PE-OH and PI₂(PI’-b-PE)-OH. (b) Bright field TEM image of OsO₄ stained PI₂(PI’-b-PE)-OH miktoarm star copolymer (sample after DSC treatment).

TEM images are projections of the respective microdomain lengths and corresponding densities through the specimen thickness. For sections of ~50 nm containing small and irregular domains, unless the domains are ordered onto a lattice, and the projected view is along a high symmetry direction, the small scale contrast variations in the image cannot be reliably interpreted.⁴⁸ Such a bright-field TEM image of the PI₂(PI’-b-PE)-OH is shown in Figure 8b, which only reinforces the lack of periodic order. Further work employing dark-field imaging of unstained samples should afford more reliable imaging of the PE crystals.⁴⁹ To improve order, the PI₂(PI’-b-PE)-OH sample was subjected to different processing. First, the sample was dissolved in xylene at 87 ℃ and then cooled down over the course of an hour to 50 ℃, the solution was kept at 50 ℃ for 5 days to allow PE crystallization, followed by cooling to room temperature
and slow evaporation of the solvent (~ 6 days). Thermal *in-situ* simultaneous small and wide-angle X-ray data was then collected to determine the crystalline character of the PE domains, their $T_m$ as well as the ODT. SAXS patterns show a broad shoulder-peak at room temperature, which nearly disappears at about 120 °C. The WAXS data shows the initial prominent 110 and 200 peaks of orthorhombic PE. These peaks disappear at about 120 °C, indicating crystal melting. Together, this data strongly suggests a melting-driven ODT just above 120 °C. The highly mobile PI matrix allows good mobility for PE block (21% by volume) to likely form chain folded crystals.

Figure 9. SAXS (a) and WAXS (b) patterns of PI$_2$(PI’-b-PE)-OH sample. The sample was heated from room temperature in increments to the temperatures indicated, held for 20 minutes at each temperature and the scattering pattern recorded. The disappearance of the shoulder in the SAXS and the 110 and 200 reflections in the WAXS, indicate a melting-induced ODT above 120 °C. This is consistent with the low degree of segregation expected between the PI and PE blocks.

By substituting PS for the PI’ mid-block, the degree of segregation increases very substantially. The degree of segregations of each pair of the polymer blocks is PI-PE: 27.5 MPa, PS-PE: 1193.7 MPa, and PI-PS: 1288.7 MPa (Table 3). To estimate the degree of segregation we use $(N_A+N_B)\times\Delta\delta^2$ where $N_A$ and $N_B$ are the respective degree of polymerization of the A and B blocks and $\Delta\delta$ is the solubility parameter difference between block A and block B. Thus, for the terpolymer star, the initial structure formed is due to the ODT between the melt miscible PI and PE blocks vs the PS block, followed by crystallization of the PE block. The SAXS and TEM results for PI$_2$(PS-b-PE)-OH suggest that an ordered hexagonal PS cylinder
phase forms. The set of 3 peaks in the PI\(_2\)(PS-\(b\)-PE)-OH SAXS data in Figure 10a correspond to \(q/q_1\) ratios close to 1, \(\sqrt{3}\) and 2, suggesting hexagonally packed cylinders. TEM images show dark/light stripe layers as well as end-on light circular features in a darker matrix (Figure 10b). Due to the junction between the PS and PE blocks, the PE crystals must lie adjacent to the PS cylinders, but our data is currently unable to reveal this finer scale structure. The proposed schematic (Figure 10c) shows chain folded PE crystals within the PI matrix surrounding the PS cylinders.

Figure 10. (a) SAXS pattern of PI\(_2\)(PS-\(b\)-PE)-OH annealed at 110 °C for 24 h. (b) Bright-field TEM image of the PI\(_2\)(PS-\(b\)-PE)-OH miktoarm star terpolymer stained with OsO\(_4\). (c) Schematic depicting the PI\(_2\)(PS-\(b\)-PE)-OH chain with the two block junctions on the surface of the PS cylinders and chain folded PE crystals in the PI matrix.

**CONCLUSION**

A novel strategy toward well-defined PE-based miktoarm star co/terpolymers, bearing an –OH group at the PE chain-end, was developed by combining two polymerization methods (anionic polymerization and polyhomologation). Initially, 4-(dichloromethylsilyl)diphenylethylene, a dual-functionality compound with two SiCl groups (linking agent) and a non-homopolymerizable double bond (diphenylethylene) was synthesized and used for linking reaction with a “living” macroanion (PI\(\text{Li}^+\)), to afford a “living” star. Subsequently, this “living” precursor was linked with BF\(_3\)OEt\(_2\) to produce boron-linked macroinitiators for the polyhomologation of dimethylsulfoxonium methylide. Oxidation/hydrolysis with TAO, led to the
formation of a series of well-defined 3-miktoarm star copolymers \((\text{PI})_2\text{PE}-\text{OH}, \text{PI}_2(\text{PI}^{-b}\text{-PE})-\text{OH}\) and terpolymer \(\text{PI}_2(\text{PS}-b\text{-PE})-\text{OH}\). Molecular characterization revealed high structural and compositional homogeneity of the final products and excellent control of all reactions involved. Microstructural characterization by SAXS, WAXS and TEM showed that the samples formed microphase separated morphologies with the star copolymers having only PI and PE components undergoing crystallization-driven microphase separation due to the low degree of segregation. Employing a much stronger segregating PS block to form a star terpolymer, induced a microphase separation transition prior to the crystallization of the PE block. The melting points of the PE components ranged from 108-113 °C with the degree of crystallinity just above 50%. The PE domains in the \((\text{PI})_2\text{PE}-\text{OH}\) and \(\text{PI}_2(\text{PI}^{-b}\text{-PE})-\text{OH}\) star samples exhibited no long-range order while the PS domains in the \(\text{PI}_2(\text{PS}-b\text{-PE})-\text{OH}\) star displayed an ordered hexagonal cylinder phase. Taking advantage of the \(\omega\)-hydroxyl group of PE segment and combined with other controlled/living polymerization methods (ROP, ATRP, RAFT), this general strategy can be further expanded for the design/synthesis of more complex PE-based macromolecular architectures (H-shaped, dendrimers etc.).

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Supporting Information
Scheme S1-S4: general reactions; Figures S1-S5: ¹H and ¹³C-NMR spectra; Figure S6: SAXS and WAXS patterns

REFERENCES


“For Table of Contents Only”

“Living stars”

Polyhomologation