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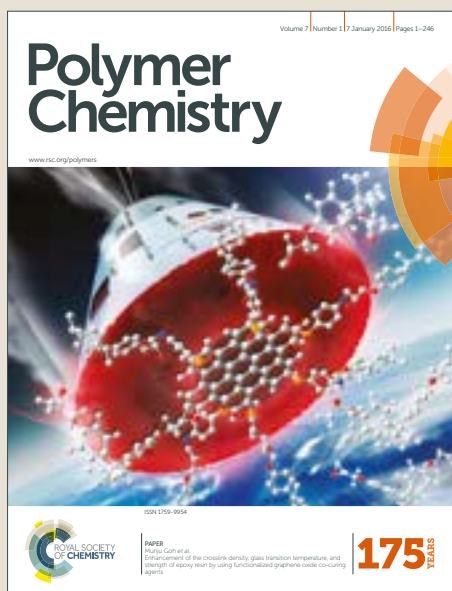
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Well-defined triblock copolymers of polyethylene with polycaprolactone or polystyrene using a novel difunctional polyhomologation initiator

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α,ω -Dihydroxy polyethylene was synthesized by polyhomologation of dimethylsulfoxonium methylide with 9-thexyl-9-BBN (9-BBN: 9-Borabicyclo[3.3.1]nonane), a novel difunctional initiator produced from 9-BBN and 2,3-dimethylbut-2-ene, with two active and one blocked sites, followed by hydrolysis/oxidation. The terminal hydroxy groups were either used directly as initiators, in the presence of 1-*tert*-butyl-2,2,4,4,4-pentakis(dimethylamino)-2 λ^5 ,4 λ^5 -catenadi(phosphazene) (t-BuP2), for the ring opening polymerization of ϵ -caprolactone to afford polycaprolactone-*b*-polyethylene-*b*-polycaprolactone (PCL-*b*-PE-*b*-PCL) or after transformation to atom transfer radical polymerization initiating sites, for the polymerization of styrene to produce polystyrene-*b*-polyethylene-*b*-polystyrene (PSt-*b*-PE-*b*-PSt) triblock copolymers. Molecular characterization by ^{11}B , ^{13}C and ^1H NMR as well as FTIR, and high temperature GPC (HT-GPC) confirmed the well-defined nature of the synthesized new difunctional initiator and triblock copolymers. Differential scanning calorimetry was used to determine the melting points of PE and PCL.

Introduction

In 2013 the global demand for the different kind of polyethylene, (High Density, Linear Low Density, Low Density) was 81.8 million tons and according to estimates it will rise to 99.6 million tons in 2018, valued 164 billion USD.¹ Polyethylene (PE) 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. Covalently linked to PE (block copolymers) polar blocks, such as polystyrene (PSt), poly(methyl methacrylate) (PMMA), polycaprolactone (PCL), poly(ethylene oxide) (PEO) and polypeptides offers significant improvements in adhesion and compatibility of PE with other polar polymers and thus broadens its applications^{2,3}. Consequently, the design/synthesis of block copolymers of PE with polar chains is important to both academia and industry.

However, the synthesis of PE/polar block copolymers by sequential addition of monomers is rather challenging since it involves two completely different and distinct polymerizations.⁴ Only a very few catalytic systems were reported to be compatible with both monomers e.g. ethylene and MMA, such as $\text{SiMe}_2(\text{Ind})_2\text{ZrMe}_2$ /methylaluminoxane(MAO)⁵ affording PE-*b*-PMMA block copolymers with polydispersity index $\text{Đ}=2.6$ and fluorenylamide-ligated titanium/MAO/ 2,6-di-*tert*-butyl-4-methylphenol leading to block copolymers with $\text{Đ}=1.25\text{--}1.56$.⁶ The mass of publications that dealing with the synthesis of PE/polar block copolymers are based on transformation (bridging) reactions between the two polymerization mechanisms.⁷ A few representative examples are given below.

A vinyl-terminated PE, synthesized by polymerization of ethylene with phenoxyimine zirconium / MAO catalytic system, was converted to atom transfer radical polymerization (ATRP) macroinitiator and used for the polymerization of styrene, MMA and *n*-butyl methacrylate to afford the corresponding block copolymers. The vinyl group functionality was 92% and the polydispersity index of the final block copolymers $\text{Đ}=1.17\text{--}1.59$ (Đ of the vinyl-functionalized PE was 1.70).⁸ A hydroxy-terminated PE, synthesized by polymerization of ethylene with $\text{Cp}^*\text{ZrCl}_2/\text{MAO}$ catalyst and oxidation of the aluminium-terminated PE, was used as

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macroinitiator for the ring opening polymerization (ROP) of caprolactone, in the presence of stannous octoate, to produce poly(ethylene-*b*-caprolactone) block copolymers ($\bar{D} = 1.73\text{--}3.23$).⁹ Fujita *et al.*¹⁰ prepared well-defined epoxy- and diol-terminated PE from vinyl-terminated PE, produced by polymerization of ethylene with bis(phenoxyimine)Zr complexes and used for the ROP of EO, in the presence of KOH, to afford (PE)(PEO)₂ and (PE)(PEO)₃ miktoarm stars (\bar{D} of the vinyl-functionalized PE was 1.80). Finally, a hydroxy-terminated PE, obtained by polymerization of ethylene with an amine-imine nickel catalyst and ZnEt₂ transfer agent, was transformed to amino-terminated PE and used as macroinitiator for the ROP of γ -benzyl-L-glutamate-N-carboxyanhydride (BLG-NCA) to afford PE-*b*-PBLG block copolymers. The polydispersity was low ($\bar{D}=1.02\text{--}1.04$) but the PE was branched.¹¹

From the above is clear that developing a new controlled/living polymerization method to synthesize well-defined PE is still needed. In 1997, Shea and co-workers, inspired from the well-known in organic chemistry homologation reaction,¹² discovered a borane initiated/mediated C1 living polymerization of dimethylsulfoxonium.¹³ This C1 polymerization, coined by Shea. Polyhomologation, has been proven as an efficient tool to synthesize well-defined and perfectly linear hydroxy-terminated polymethylene (equivalent to PE). The general mechanism involves the formation of an organoboron "ate" complex (zwitterionic intermediate) formed by attack of the nucleophilic dimethylsulfoxonium methylide (monomer) on the Lewis acidic borane (initiator) followed by migration/insertion of -CH₂- into the initiator. As a consequence, the methylene groups are randomly inserted one by one (C1 polymerization) into the three arms of the initiator leading to a 3-arm polymethylene star with boron at the junction point. After oxidizing/hydrolyzing the 3-arm boron star, an OH-terminated polymethylene (polyethylene) is obtained.¹⁴ The OH-terminated PE can be used either as macroinitiator for ROP of cyclic ethers/esters or for living/radical polymerization after transformation, to afford well defined PE/polar block copolymers with perfectly linear PE and high molecular weight homogeneity.^{15–20} In addition, the PE-OH can be transformed to norbornene-macromonomer and participate in ring opening metathesis polymerizations.^{21–23}

Along these lines we report in this paper the synthesis of 9-thexyl-9-BBN (9-BNN: 9-Borabicyclo[3.3.1]nonane), a novel difunctional polyhomologation initiator and its use for the

production of triblock copolymers of polyethylene with polycaprolactone, a biocompatible/biodegradable polymer with many biomedical applications and polystyrene, a very important commercial polymer, by combining polyhomologation with ROP or ATRP. The only difunctional polyhomologation initiator, until now, was a B-thexyl-cyclohexene borocane proposed by Shea *et al.*²⁴

Experimental Section

Materials

Tetrahydrofuran (THF) and toluene (Fischer Scientific) were refluxed over sodium/benzophenone and distilled under a nitrogen atmosphere just before use. All other chemicals were purchased from Sigma-Aldrich. Phosphazene superbases 1-*tert*-Butyl-2,2,4,4,4-pentakis(dimethylamino)-2 λ 5,4 λ 5-catenadi-(phosphazene) (*t*-BuP2; 2 M solution in THF) and acetic acid (99.7%) were used as received. ϵ -Caprolactone (ϵ -CL; 99%) was dried over calcium hydride at room temperature for 48 h and distilled under reduced pressure just before use. Allylmagnesium bromide solution in THF (1.0 M), copper (I) bromide (99.999%), pentamethyldiethylenetriamine (PMDETA, 99%), 2,3-dimethylbut-2-ene ($\geq 99\%$), trimethylamine N-oxide dihydrate (TAO \cdot 2H₂O) ($\geq 99\%$), were used as received. Styrene ($\geq 99\%$) was distilled over calcium hydride under reduced pressure. Dimethylsulfoxonium methylide was prepared according to Corey's method followed by switching the solvent from THF to toluene.²⁵

Instruments

The high temperature gel permeation chromatography (HT-GPC) measurements were carried out at 150 °C with the Agilent PL-GPC 200 instrument equipped with one PLgel 10 μ m Mixed-B column and a differential refractive index (DRI) detector. 1,2,4-Trichlorobenzene (TBC) was the eluent at a flow rate of 1.0 mL/min. The system was calibrated with PSt standards. The ¹H NMR, ¹³C NMR, ¹¹B NMR spectra were recorded on a Bruker AVANCE III-600 in toluene-*d*₈ at 25 °C. Fourier transform infrared (FT-IR) spectra were recorded using Nicolet iS10 FT-IR spectrometer from Thermo Scientific. Differential scanning calorimetry (DSC) characterization was performed on a Mettler Toledo DSC1/TC100 system in an inert nitrogen atmosphere. The second heating curve was used to determine the melting temperature (*T*_m).

Synthesis of initiator 9-thexyl-9-BBN

A 50 mL round bottom flask equipped with a magnetic stir bar was degassed three times using vacuum line and then was filled with argon. Under Argon flow, 1 ml of dry THF was introduced into the flask via a syringe, then an ice bath was placed under the flask. After 10 min, 0.5 ml (3.7 mmol) of 9-BBN solution (5.0 M in THF) was introduced, followed by the addition of 0.045 ml (0.38 mmol) of 2,3-dimethylbut-2-ene via a glass syringe, then the reaction was left for 3 to 4 h. Finally, the THF was distilled and the initiator was used immediately.

Synthesis of polycaprolactone-*b*-polyethylene-*b*-polycaprolactone

Freshly prepared 9-thexyl-9-BBN (difunctional initiator) was introduced into a 50 mL round bottom flask containing the monomer dimethylsulfoxonium methylide and equipped with a magnetic stirring bar. The flask was previously degassed three times using vacuum line and filled with argon. The mixture was stirred at 80 °C for an hour. Then, TAO was added to the mixture and stirred for 2 h at 80 °C to afford α,ω -dihydroxy polyethylene, macroinitiator for the ring opening polymerization of ϵ -CL. In a separate flask 0.10 g of the macroinitiator was dissolved in distilled toluene in an argon flow at 80 °C, followed by the addition of 0.13 ml of *t*-BuP₂ solution (0.26 mmol). The mixture was stirred until the α,ω -dihydroxy polyethylene, the (macroinitiator) and *t*-BuP₂ (catalyst) were completely dissolved, then 3.0 ml of ϵ -CL monomer (27 mmol) was added to start the polymerization. The reaction was quenched after 24 h by addition of acetic acid, and the solution was poured into cold methanol to precipitate the polymer. The white powder was then collected, dried in vacuum and used for HT-GPC, ¹H NMR, FTIR and DSC. Conv. (ϵ -CL) = 75%, $M_{n,theor}$ (PE) = 1400 g.mol⁻¹, $M_{n,theor}$ (PCL) = 22800 g.mol⁻¹, $M_{n,theor}$ (PCL-*b*-PE-*b*-PCL) = 24200 g.mol⁻¹, $M_{n,SEC}$ (PE) 2300 g.mol⁻¹, $M_{n,SEC}$ (PCL-*b*-PE-*b*-PCL) = 16000 g.mol⁻¹, \bar{D} (PCL-*b*-PE-*b*-PCL) = 1.2. ¹H NMR (600 MHz, toluene-*d*₈, 80 °C) (Figure 4 b) 3.95-4.1 ppm (-CH₂OOC-) 3.38 ppm (m, 2H, CH₂-OH, end group of PE), 2.23 ppm (C=OCH₂ of PCL), 1.40-1.36 ppm (CH₂ of PE). $M_{n,NMR}$ (PE) = 2500 g.mol⁻¹, $M_{n,NMR}$ (PCL) = 21000 g.mol⁻¹, $M_{n,NMR}$ (PCL-*b*-PE-*b*-PCL) = 23500 g.mol⁻¹.

Synthesis of macroinitiator Br-PE-Br

In a typical procedure, 0.346 g HO-PE-OH was dissolved in 40 mL of dry toluene, followed by introduction of triethylamine (0.168 mL, 1.66 mmol) via a syringe. 2-bromo-2-methyl propionyl bromide (0.214 mL, 0.930 mmol) was added to the vigorously stirred

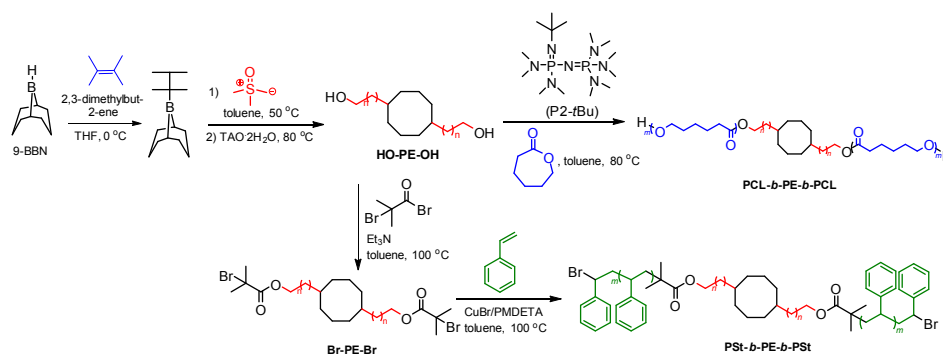
solution. The reaction mixture was stirred at 100 °C temperature for 10 hours. The precipitated by-product was removed by filtration, and the solution was poured into methanol to precipitate the product. The resulting off-white solid Br-PE-Br was dried in vacuum at 35 °C for 24 h. ¹H NMR (600 MHz, toluene *d*₈) (Figure S1, SI) 1.93 ppm (-C(CH₃)₂Br) and 4 ppm (-CH₂O-). In the SEC trace of OH-PE-OH (Figure 5b), a shoulder (~5% of the total area) at approximately twice the molecular weight is observed. The origin of this peak is due in the presence of traces of adventitious oxygen during the oxidation step with TAO. Macroradicals generated in this way have been used to initiate the polymerization of other vinyl monomers towards the synthesis of copolymers. In the absence of vinyl monomers these macroradicals can produce higher molecular weight chains by combination.²⁶

Synthesis of polystyrene-*b*-polyethylene-*b*-polystyrene

A typical ATRP procedure is given below. Toluene (5.0 ml), CuBr (2.6 mg, 0.018 mmol) and styrene (0.45 ml, 3.9 mmol) were placed in a 50 ml Schlenk flask. The mixture was subjected to three freeze-pump-thaw cycles. The ATRP was carried out using Br-PE-Br as macroinitiator, N,N,N',N',N''-pentamethyl diethylene triamine (PMDETA) as catalyst/ligand system in toluene. This process was done at 100 °C to ensure the polyethylene is totally soluble. The reaction was terminated after 24 hours by adding acetic acid. Finally, the solution was added into cold methanol to precipitate the polymer. The formation of the triblock copolymer was verified by HT-GPC, DSC, ¹H NMR and FTIR. $M_{n,theor}$ (PE) = 1400 g.mol⁻¹, $M_{n,theor}$ (PSt) = 20800 g.mol⁻¹, $M_{n,theor}$ (PSt-*b*-PE-*b*-PSt) = 22200 g.mol⁻¹, $M_{n,SEC}$ (PE) = 2500 g.mol⁻¹, $M_{n,SEC}$ (PSt-*b*-PE-*b*-PSt) = 34000 g.mol⁻¹, \bar{D} (PSt-*b*-PE-*b*-PSt) = 1.2. ¹H NMR (600MHz, Toluene-*d*₈, 80 °C) 6.4-7.3 ppm (aromatic proton of styrene). 3.38 ppm which disappeared after the preparation of the macroinitiator, (m, 2H, CH₂-OH, end group of PE), 1.40-1.36 ppm (CH₂ of PE). $M_{n,NMR}$ (PE) = 2500 g.mol⁻¹, $M_{n,NMR}$ (PSt) = 19000 g.mol⁻¹, $M_{n,NMR}$ (PSt-*b*-PE-*b*-PSt) = 21600 g.mol⁻¹, \bar{D} (PSt-*b*-PE-*b*-PSt) = 1.2.

Result and Discussion

The general reactions for the synthesis of the new difunctional initiator 9-thexyl-9-BBN, the intermediate macroinitiators α,ω -dihydroxy polyethylene and α,ω -dibromo polyethylene, as well as the final triblock copolymers PCL-*b*-PE-*b*-PCL and PSt-*b*-PE-*b*-PSt are given in Scheme 1.



Scheme 1 General reactions for the synthesis of 9-thexyl-9-BBN, α,ω -dihydroxy polyethylene, α,ω -dibromo polyethylene, PCL-*b*-PE-*b*-PCL and PSt-*b*-PE-*b*-PSt

The initiator 9-thexyl-9-BBN, containing two initiating sites and one blocked for polyhomologation, was synthesized by reacting 2,3-dimethylbut-2-ene and 9-BBN in THF at 0 °C. The successful synthesis was confirmed by ^{11}B , ^1H and ^{13}C NMR in d_8 -toluene, a non-coordination solvent, at room temperature. The ^{11}B NMR spectrum of 9-BBN shows a peak at 27.8 ppm. This peak was shifted to 33.4 ppm for 9-thexyl-9-BBN indicating the presence of the thexyl group (Figure 1). The ^1H NMR spectrum of the 9-BBN exhibits peaks at 1.44–1.57 ppm (m, 4 H), 1.58–1.74 ppm (m, 12 H) and 1.83–2.07 ppm (m, 12 H) while the spectrum of 9-thexyl-9-BBN shows two new peaks from 0.8 to 1.0 ppm characteristics of the thexyl moiety (Figure 2). The ^{13}C NMR spectrum of the 9-BBN exhibits peaks at 20.2 ppm CH (C-1,5), 24.3 ppm CH $_2$ (C-3,7), 33.6 ppm CH $_2$ (C-2,4,6,8). In the case of 9-thexyl-9-BBN the ^{13}C NMR spectrum shows two new peaks at 40.5 ppm (C-B), 34–34.5 ppm (CH), characteristics of the thexyl group (Figure 3).

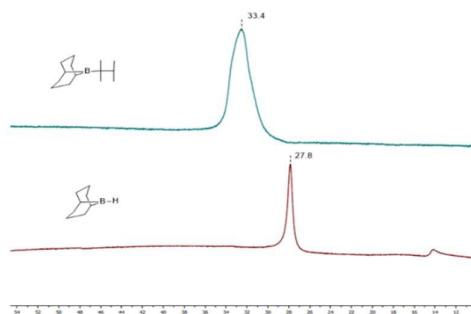


Figure 1. ^{11}B NMR spectra of 9-BBN and 9-thexyl-9-BBN in toluene- d_8 at 25 °C (600 MHz).

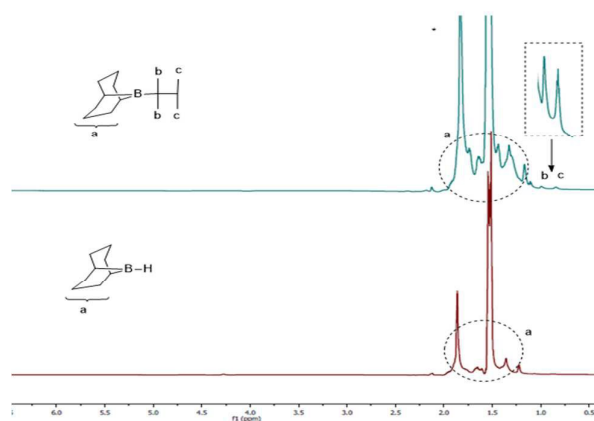


Figure 2. ^1H NMR spectra of 9-BBN and 9-thexyl-9-BBN in toluene- d_8 at 25 °C (600 MHz)

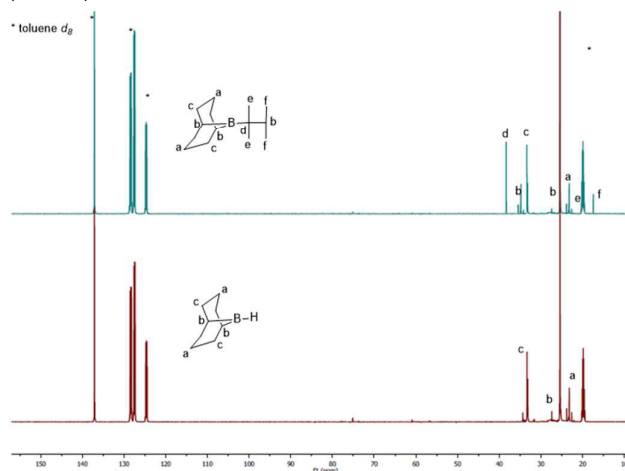


Figure 3. ^{13}C NMR spectra of 9-BBN and 9-thexyl-9-BBN in toluene- d_8 at 25 °C (600 MHz)

The 9-thexyl-9-BBN was used to initiate the polyhomologation of dimethylsulfoxonium methylide to afford α,ω -dihydroxy polyethylene (HO-PE-OH), which was used on one hand, as difunctional macroinitiator for the ring opening polymerization of ϵ -caprolactone in the presence of t -BuP₂, to produce polycaprolactone- b -polyethylene- b -polycaprolactone (PCL- b -PE- b -PCL) and on the other hand, after transformation of the OH- to -Br (reaction with 2-bromoisobutryl bromide) to initiate the ATRP of styrene and afford polystyrene- b -polyethylene- b -polystyrene (PSt- b -PE- b -PSt). The successful syntheses of PCL- b -PE- b -PCL and PSt- b -PE- b -PSt were confirmed by ¹H NMR and GPC. As shown in Figure 4a, the characteristic chemical shifts of polyethylene at $\delta = 1.4$ ppm (-CH₂-) and of the terminal -CH₂OH groups at $\delta = 3.4$ ppm are present. After ROP or ATRP, the fingerprint of PCL and PSt are shown in Figure 4b and 4c, respectively. From the integration of the

appropriate protons, the calculated molecular weights of HO-PE-OH, PCL- b -PE- b -PCL and PSt- b -PE- b -PSt were 2500, 23500 and 21600, respectively. The theoretical molecular weights of triblock copolymers were 24200 (PCL- b -PE- b -PCL) and 22200 (PSt- b -PE- b -PSt), in good agreement with the experimental determined molecular weights. In Figure 5 the SEC traces of the macroinitiator and the corresponding triblock copolymer are given. The peak corresponding to the triblock copolymer PCL- b -PE- b -PCL ($\bar{M}_n = 1.2$) shifted to a higher molecular weight compared to the precursor polymer HO-PE-OH ($\bar{M}_n = 1.2$). In the case of PSt- b -PE- b -PSt, the same trend was observed ($\bar{M}_n = 1.2$). In the case of PSt- b -PE- b -PSt the small peak with higher molecular weight maybe is due to the coupling of macroradicals during the ATRP.

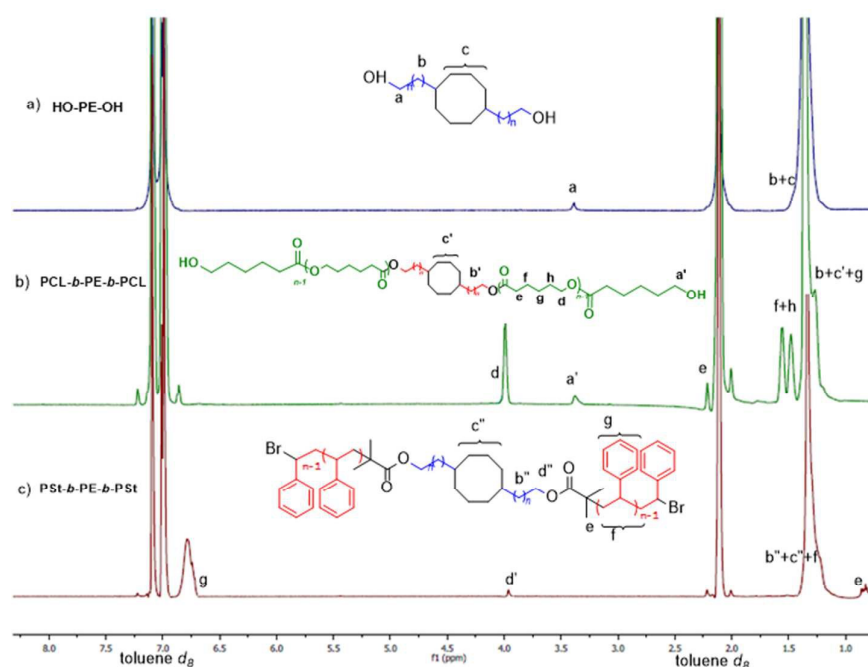


Figure 4. ¹H NMR spectra of (a) α,ω -dihydroxy polyethylene, (b) PCL- b -PE- b -PCL and (c) PSt- b -PE- b -PSt in toluene- d_8 at 80 °C (600 MHz).

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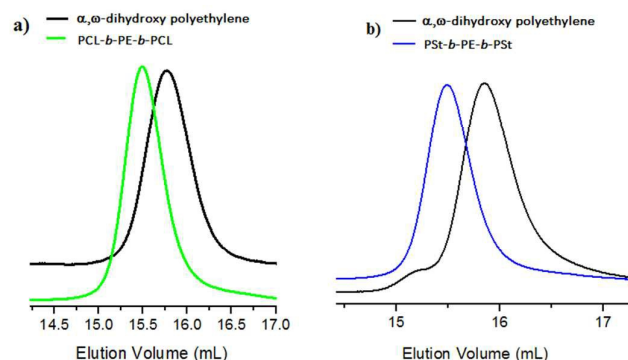


Figure 5. HT-SEC (TCB at 150 °C, PSt standard) traces of α,ω -hydroxy polyethylene and (a) PCL-*b*-PE-*b*-PCL, (b) PSt-*b*-PE-*b*-PSt

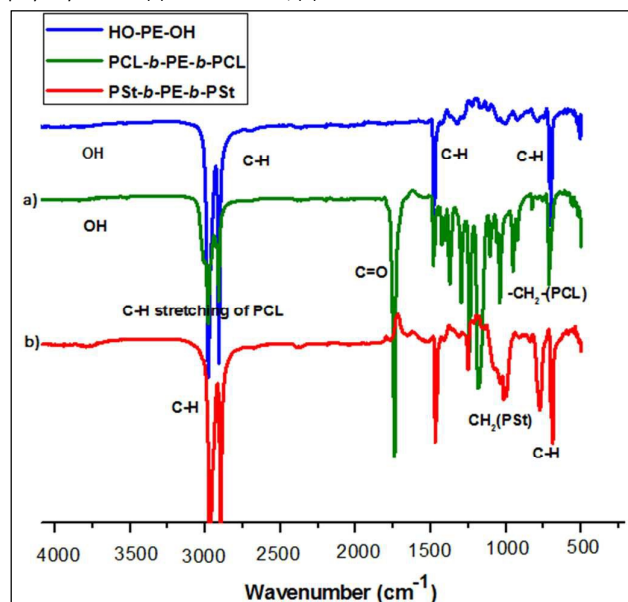


Figure 6. FT-IR spectra of α,ω -hydroxy polyethylene along with the corresponding a) PCL-*b*-PE-*b*-PCL and b) PSt-*b*-PE-*b*-PSt triblock copolymers.

Further evidence for the successful synthesis of the triblock copolymers was provided by FT-IR spectroscopy. In Figure 6 (top spectrum) the characteristics bands of polyethylene are present 3000-2800, 1550-1400 and 750-650 cm^{-1} . After the ROP of the ϵ -CL new peaks were appeared at 1721 cm^{-1} , attributed to the stretching vibration of carbonyl groups (C=O) of PCL and at 1165–1468 cm^{-1} ,

assigned to the deformation of $-\text{CH}_2-$ of PCL (Figure 6a). Similarly, after the ATRP of St, new absorption bands are appeared at 1025 cm^{-1} ($-\text{CH}_2-$ of PSt) and at 699-750 cm^{-1} related to C-H bending of aromatics of PSt (Figure 6b).

The HO-PE-OH, PCL-*b*-PE-*b*-PCL and PSt-*b*-PE-*b*-PSt were also analyzed by DSC under a nitrogen atmosphere. In Figure 7, HO-PE-OH curve shows only one peak at 128 °C corresponding to PE. The thermograph of PCL-*b*-PE-*b*-PCL reveals two peaks corresponding to the melting points of PCL (50 °C) and PE (110 °C), another evidence of the successful synthesis of the triblock copolymer of PCL and PE. In the case of PSt-*b*-PE-*b*-PSt, there is only one peak around 125 °C corresponding to the melting temperature of PE, since the T_g of PSt is masked by the peak of PE.

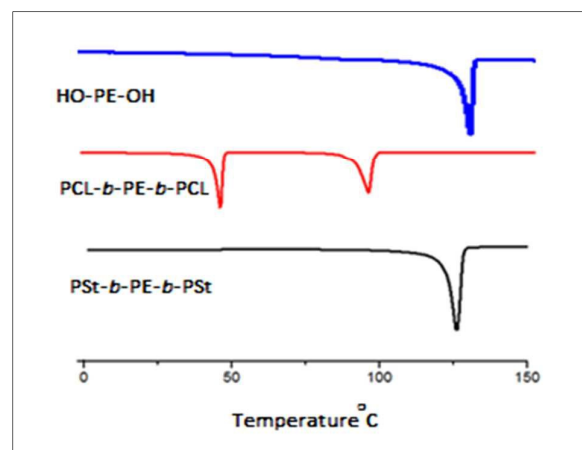


Figure 7 DSC traces of HO-PE-OH, PCL-*b*-PE-*b*-PCL and PSt-*b*-PE-*b*-PSt (N₂, 10 °C/min, second cycle).

Conclusion

A new difunctional polyhomologation initiator was successfully synthesised as proved by ^{11}B , ^{13}C and ^1H NMR spectroscopy. This initiator was used for the synthesis of triblock copolymers of PE with PCL and PSt. The synthesized copolymers are well-defined as proved by HT-GPC, ^1H NMR, DSC and FTIR. This initiator opens new horizons towards the synthesis of PE-based complex macromolecular architectures with industrially important polar

monomers, such as caprolactone, lactides, methacrylates, styrene, peptides, etc.

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TOC

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