Anionic polymerization and polyhomologation: an ideal combination to synthesize polyethylene-based block copolymers

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Experimental section

Chemicals

s-Butyllithium (*s*-BuLi) (1.4 M in cyclohexane, Aldrich), *n*-butyllithium (*n*-BuLi) (1.6 M in hexane, Aldrich), *di*(*n*-butyl)magnesium (2.5M in cyclohexane, Aldrich), calcium hydride (CaH_2) (95%, Aldrich), trimethylsulfoxonium iodide (98%, Alfa Aesar), Benzyltri-*n*-butylammonium chloride (98%, Alfa Aesar) and trimethylamine *N*-oxide dihydrate (TAO) (>99%, Fluka) were used as received. Styrene and butadiene were purchased from Aldrich and distilled from CaH_2 before use. Boron trifluoride diethyl etherate (BF_3OEt_2) (purum, Fluka) was distilled from CaH_2 before use. Sodium hydride (60% dispersion in mineral oil, Acros) was washed with petroleum ether (40-60 ºC) before use. Methanol (99%, Fisher), acetonitrile (99%, Fisher), dichloromethane (>99%, Fisher) were obtained from Fisher and used as received. Tetrahydrofuran (99%, Fisher) and toluene (99.7%, Fluka) were distilled from CaH_2 before use. PE standard for FTIR with molecular weight of 2000 was purchased from Aldrich.

Instruments

High temperature size exclusion chromatography (HT-SEC) measurements were carried out on a Viscoteck HT-GPC module 350 instrument with two PLgel 10 μm MIXED-B columns using 1,2,4-trichlorobenzene (TCB) as eluent at a flow rate of 0.8 mL/min at 150 ºC. The system was calibrated by PS standards. SEC curves at 35 ºC were recorded on a Viscoteck 305 instrument with a column of PLgel 10 μm MIXED-C column (only used for measurement of $(PS)_3B$) or two columns of Styragel HR2 THF (7.8×300 mm) and Styragel HR4 THF (7.8×300 mm). THF was used as eluent at flow rate of 1 mL/min. The system was calibrated by PS standards before use. The samples of boron-linked 3-armed star polymers of $(PBd)_3B$ and $(PS)_3B$ for SEC were prepared in a glove box to protect the borane species from air. ^1H and solid state ^{13}C NMR spectra were recorded on a Bruker AVANCE III-600 spectrometer.

Fourier-transformed infrared spectroscopy (FTIR) (transmission) measurements were performed on a Nicolet Magna 6700 FT spectrometer. Upper critical solution temperatures (UCST) of PBd-*b*-PE and PS-*b*-PE solution in toluene (3 mg/mL) were determined by UV-Vis on an Evolution 600 instrument with a manual temperature controller. Exact molecular weight of PBd was determined on an Ultraflex MALDI-ToF machine (Bruke) using innovative smartbeam-II™ laser. Dithranol (20 mg/mL in THF) and silver trifluoroacetate (10 mg/mL in THF) were used for the PBd sample (10 mg/mL in THF) with volumes of 10 μL, 2.0 μL and 10 μL, respectively. Differential scanning calorimetry (DSC) was performed on a Mettler Toledo DSC1/TC100 system in an inert nitrogen atmosphere. The samples were heated from room temperature to 150 ºC, cooled to -150 ºC (for PBd-*b*-PE) or -120 ºC (for PS-*b*-PE) and finally heated again to 150 ºC at a heating/cooling rate of 10 ºC/min. The second heating curve was used to determine the glass transition temperature (T_g), melting temperature (T_m) and degree of crystallinity.

Experiments

Preparation of boron-linked 3-armed star-like macroinitiators

All the flasks were connected on a vacuum line, heated with a heat gun and dried with argon/vacuum for more than 5 times. In a typical process, 1 mL of *s*-BuLi (1.3 M in cyclohexane) was added to the reaction flask and then pump to high vacuum. Cyclohexane (50 mL) was distilled to the reaction flask from PSLi solution at room temperature under high vacuum and melted at 10 ºC. Butadiene (10 mL) was dried by dibutylmagnesium under vacuum at -20 ºC for 0.5 h and distilled to the reaction flask using an ice bath. The reaction solution was warmed to room temperature and stirred overnight. After polymerization, 10 mL solution was taken out and quenched by degased methanol followed by precipitation in 100 mL of methanol resulting in a white sticky precipitate which was dried under vacuum, protected from light for measurement ($M_{n\ \mathrm{MALDI}} = 5.9 \times 10^3$, Figure S1, $M_{n\ \mathrm{SEC}} = 12.7 \times 10^3$, $\mathrm{PDI}_{\mathrm{SEC}} = 1.05$). To the rest of the solution 0.35 mL of BF_3OEt_2 solution in diethyl ether (0.7 M) was slowly added and stirred for 3 days at room temperature protecting from light to afford macroinitiator, $(PBd)_3B$. Using the same method, $(PS)_3B$ has been prepared.

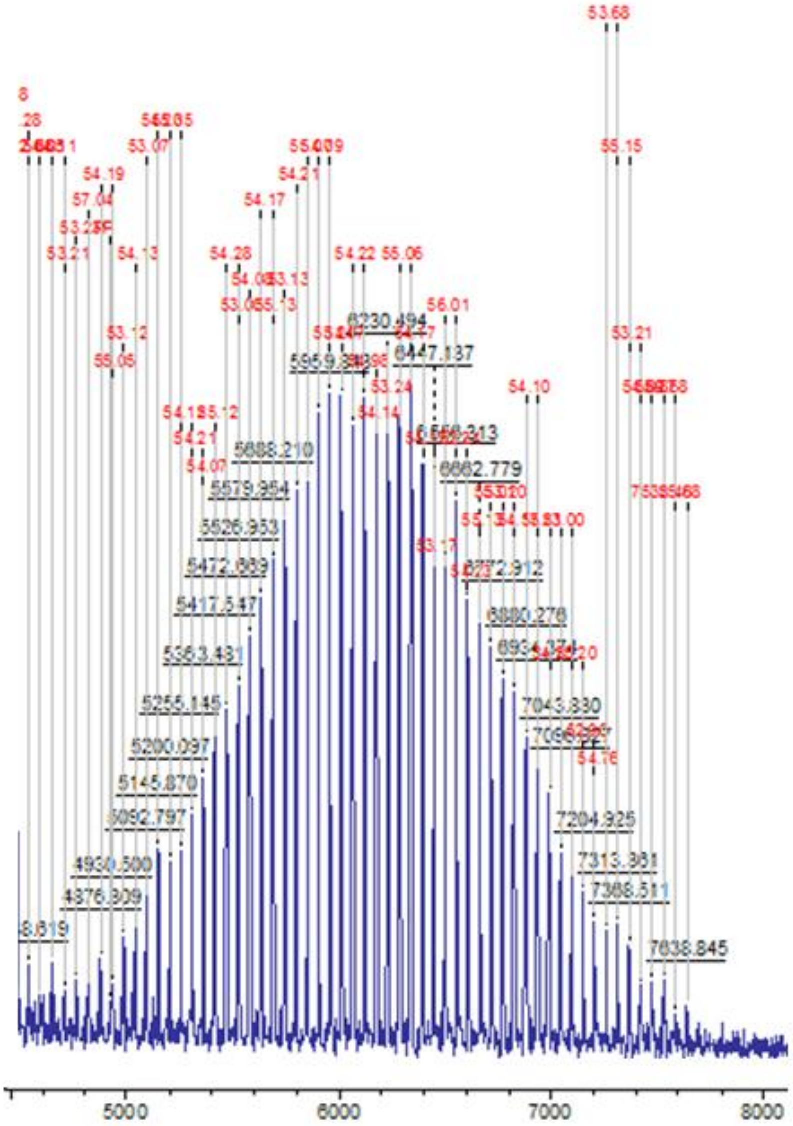

Figure S1 MALDI-ToF mass spectrum of PBd (right) (M_n=5888)

Preparation of trimethylsulfoxonium chloride

42.8 g of trimethylsulfoxonium iodine was added into a biphase mixture of dichloroform (330 mL) and water (440 mL), followed by introduction of 65.8 g of tributylbenzylamino chloride. The mixture was stirred at room temperature, protected from light, for 24 h. Aqueous phase was collected and washed by CH_2Cl_2 (60 mL × 3). After removal water on a rotary evaporator, white needle-like crystal was obtained. The crystal was dissolved in methanol at 50 ºC, and then cooled to room temperature naturally, followed by cooling to 4 ºC in fridge overnight. A needle-like crystal product of trimethylsufoxonium chloride (21 g, yield: 84%) with a high purity (>99%) was obtained and confirmed by ^{1}H and ^{13}C NMR in DMSO-*d6*.

Preparation of dimethylsulfoxonium methylide in THF [1]

To a three-necked flask connected with a condenser and argon/vacuum line, 6.8 g of NaH (dispersed in mineral oil, 60% in weight) was introduced and washed with dry petroleum ether (20 mL × 3). The residual solvent was removed under vacuum. 20 g of dry trimethylsulfoxonium chloride was added, followed by 200 mL of THF. All the operation was performed under argon flow. The mixture was heated and refluxed at 70 ºC until the gas ceased in 4-5 hours. After reaction, THF was removed under low pressure followed by adding 50 mL of dry toluene. The solution was filtered by dry celite-545 aid (2-3 cm). The flask and filtration cake was washed with 200 mL fresh toluene. A clear solution with a light yellow color was obtained. The concentration of 0.73 mmol/mL (yield: 73%) was titrated by standard HCl aqueous solution.

Polyhomologation of dimethylsulfoxonium methylide by the macroinitiators

In a typical process, to 20 mL of PS_3B solution in cyclohexane (0.056 mmol), 150 mL of ylide solution (0.26 M) in toluene was added and heated to 80 ºC. 1 h later, 1 mL of the reaction mixture was taken out and added into 50 mL water, pH=7-8 was qualitatively determined by a pH indicator paper. 0.2 g of trimethylaminoxygen dihydrate was added into the reaction mixture and kept stirring for 3 h at 70 ºC. The reaction solution was concentrated on a rotatory evaporator. The resulting concentrated solution was heated to be clear and transparent and was dropped into 200 mL of acetonitrile to give a white powder product which was washed with methanol and acetone. To fractionate the product, 0.7 g of product was dissolved in 50 mL of toluene at high temperature and cooled to room temperature followed by adding a little acetone (*ca.* 5 mL) slowly and cooled to -20 ºC. After centrifuged at 7000 rps (30 min × 3), a gel-like product was found in the bottom. The purification was carried out two or three times until there was not any PS resident left in HT-SEC curves. 0.2 g of pure product, PS-*b*-PE was obtained after purification. In the same method, PBd-*b*-PE has been prepared.

Reference

1 E. J. Corey, M. Chaykovsky. *J. Am. Chem. Soc.* 1965, **87**, 1353-1364