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Synthesis of Well-Defined Polyethylene-Based 3-Miktoarm Star Copolymers and Terpolymers

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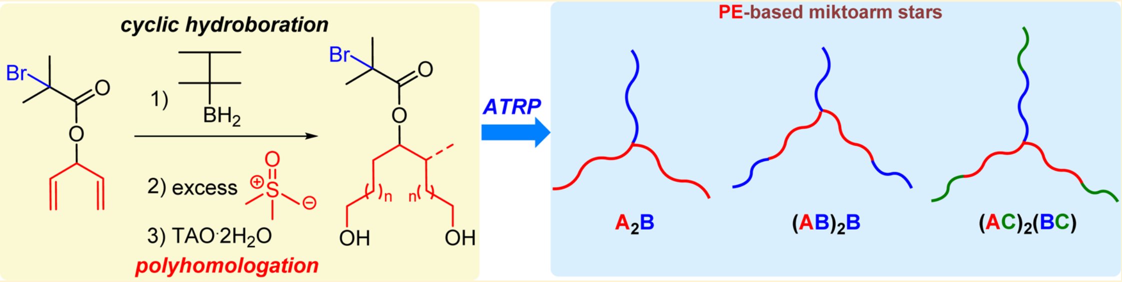
Supporting Information



ABSTRACT: Novel polyethylene (PE)-based 3-miktoarm star copolymers A_2B, $(AB)_2B$ and terpolymers $(AC)_2(BC)$ [A: PE; B, C: polystyrene (PS) or poly(methyl methacrylate) (PMMA)] were synthesized by combining boron chemistry, polyhomologation, and atom transfer radical polymerization (ATRP). 1,4-Pentadiene-3-yl 2-bromo-2-methylpropanoate was first synthesized followed by hydroboration with thexylborane to afford B-thexylboracyclanes, a multi-heterofunctional initiator with two initiating sites for polyhomologation and one for ATRP. After polyhomologation of dimethylsulfoxonium methylide the α,ω-dihydroxyl polyethylene $(PE\text{-}OH)_2\text{-}Br$ produced served as macroinitiator for the ATRP of styrene to afford $(PE\text{-}OH)_2\text{-}(PS\text{-}Br)$. Both $(PE\text{-}OH)_2\text{-}Br$ and $(PE\text{-}OH)_2\text{-}(PS\text{-}Br)$ were transformed to two new trifunctional macroinitiators $(PE\text{-}Br)_2\text{-}Br$ and $(PE\text{-}Br)_2\text{-}(PS\text{-}Br)$ through esterification reactions and used for the synthesis of $(AB)_2B$ and $(AC)_2(BC)$ 3-miktoarm star co/terpolymers. All intermediates and final products were characterized by ^1H NMR, high temperature gel permeation chromatography (HT-GPC), and differential scanning calorimetry (DSC). The synthetic method is a general one and can be used for the synthesis of complex PE-based architectures by combination with other living/living-controlled polymerization techniques.

■ INTRODUCTION

Miktoarm (mikto from the greek word *μικτός*, meaning mixed)[1] star polymers, which contain chemically different arms, have attracted considerable attention in past decades. Because of their unique chemical structure, they have been used in many studies including drug delivery,[2] micellization,[3] and bulk self-assembly.[4] One of the most established synthetic methods for miktoarm stars is based on anionic polymerization high vacuum techniques and the use of appropriate linking agents such as divinylbenzenes, double 1,1-diphenylethylenes, or chlorosilanes.[5] Through the chlorosilane protocol a plethora of miktoarm stars were synthesized including AB_2, ABCD, etc., where A, B, C, and D are PS, polyisoprene, polydimethylsiloxane, poly(2-vinylpyridine), etc.[5a−d] The synthesis of PE-based miktoarm stars is very important since PE is one of the most common industrial polymers thanks to its excellent physical properties and easy processability. A way toward these materials is the synthesis of polybutadiene (PBd) stars followed by hydrogenation to afford the PE-stars. Unfortunately, the maximum 1,4 microstructure of PBd by anionic polymerization is 93%, and consequently the PE synthesized by this method is contaminated by 7% butene units.[6]

A very few examples dealing with the synthesis of PE-based star polymers directly from ethylene catalytic polymerization, theoretically leading to 100% PE, can be found in the literature. For example, a trinuclear Pd−diimine complex was used for the "living" polymerization of ethylene to afford well-defined 3-arm star PE.[7] Another example is the synthesis of hydroxyl-terminated PE followed by "click" chemistry or ATRP to produce the miktoarm star.[8] The difficulty associated with the catalytic ethylene polymerization is the lack of efficiency to produce end-functionalized PEs, which are intermediates for the synthesis of miktoarm stars in combination with other polymerization techniques.[9] Therefore, it is clear that more powerful methods are needed toward the synthesis of PE-based polymeric materials.

Polyhomologation, an alkylborane-initiated polymerization of dimethylsulfoxonium methylide developed by Shea et al.,[10] is a powerful tool for the synthesis of well-defined linear polymethylenes (polymethylene, PM, equivalent to PE) without side

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alkyl groups. Well-defined PE-based linear, cyclic, and brush polymers have been synthesized by polyhomologation or by combination with other living or controlled/living polymerization techniques.[11,12] For example, 3-arm PE homostars were synthesized by polyhomologation followed by a "stitching reaction" or polyhomologation initiated by 1-boraadamantane.[13] In the case of miktoarm stars, the only examples given in the literature are the PE-PS$_2$ and PE-PMMA$_2$ 3-miktoarm stars synthesized by combining polyhomologation and ATRP.[14]

Recently, we reported a strategy based on polyhomologation initiated by B-thexylsilaboracyclic derivatives, having two silicon-connected initiating sites and one blocked, for the synthesis of PE-based 3-miktoarm star PE$_2$-PS, 4-arm PE homostars, and PE-branched double graft copolymers.[15] In this paper, a novel multi-heterofunctional initiator is presented for the synthesis of A$_2$B, (AB)$_2$B, and (AC)$_2$(BC) (A, PE chain; B, C: PS or PMMA chain) 3-miktoarm star co/terpolymers using the "core-first" strategy[16] and a combination of polyhomologation with ATRP.[17]

■ EXPERIMENTAL SECTION

Materials. Ethyl formate (97%), vinylmagnesium chloride solution (1.6 M in THF), copper(I) bromide (99.999%), pentamethyldiethylenetriamine (PMDETA, 99%, Aldrich), 2,3-dimethylbut-2-ene (⩾99%), trimethylamine *N*-oxide dihydrate (TAO·2H$_2$O) (⩾99%, Aldrich), borane dimethyl sulfide complex solution (5.0 M in diethyl ether), 2-bromoisobutyryl bromide (BIBB, 98%), and pyridine (99.8%) were purchased from Aldrich and used as received. Methyl methacrylate (99%) and styrene (⩾99%) were distilled over calcium hydride under reduced pressure. Tetrahydrofuran and toluene were refluxed over sodium/benzophenone and distilled under a nitrogen atmosphere just before use. Dimethylsulfoxonium methylide was prepared according to Corey's method followed by switching the solvent from THF to toluene.[18] Thexylborane was prepared by adding 2,3-dimethylbut-2-ene to borane dimethyl sulfide complex solution (5.0 M in diethyl ether) in THF at 0 °C.[19]

Measurements. The high temperature gel permeation chromatography (HT-GPC) measurements were carried out at 150 °C with the Agilent PL-GPC 220 instrument equipped with one PLgel 10 μm MIXED-B column and a differential refractive index (DRI) detector. 1,2,4-Trichlorobenzene (TCB) was the eluent at a flow rate of 1.0 mL/min. The system was calibrated with PS standards. Triple-detection HT-GPC measurements were carried out on a Viscoteck HT-GPC module 350 instrument with two PLgel 10 μm MIXED-B columns equipped with a refractive index, a light scattering ($\lambda = 670$ nm), and a viscometry detector. TCB was used as an eluent (0.8 mL/min) at 150 °C. The tridetector HT-GPC system was calibrated with PS standard ($M_w = 115 \times 10^3$ g/mol, PDI = 1.05). The ^{1}H and ^{13}C NMR spectra were recorded with a Bruker AVANCE III-500 or 600 spectrometer. DSC measurements were performed using a Mettler Toledo DSC1/TC100 system under an inert atmosphere (nitrogen). The sample was heated from room temperature to 150 °C, cooled to −10 °C, and finally heated again to 150 °C with a heating/cooling rate of 10 °C/min. The second heating curve was used to determine the glass transition temperature (T_g), melting temperature (T_m), and degree of crystallinity. The crystallinity X_c of the samples was derived from $X_c = \Delta H_m/\Delta H_m^+$, where ΔH_m (288 kJ kg^{-1}) is the specific enthalpy of melting for 100% crystalline PE.[20]

Synthesis of 1,4-Pentadiene-3-yl 2-Bromo-2-methylpropanoate. Ethyl formate (4.0 mL, 0.050 mol) was added dropwise to a solution of vinylmagnesium chloride solution (63 mL, 0.10 mol, 1.6 M in THF) in dry THF (30 mL) at 0 °C under argon (Ar). After completion of the addition, the mixture was kept under stirring for further 1 h at room temperature. Then the reaction was quenched with saturated NH$_4$Cl solution (30 mL), and the mixture was extracted with ethyl acetate (20 mL × 3). The combined organic extracts were washed with brine, dried over MgSO$_4$, filtered, and concentrated to give the crude 1,4-pentadien-3-ol as a yellow oil.

Pyridine (2.2 mL, 28 mmol) and 2-bromoisobutyryl bromide (3.4 mL, 28 mmol) were added to a solution of crude penta-1,4-dien-3-ol (2.1 g, ∼ 25 mmol) in THF (50 mL) at 0 °C under Ar. The mixture was stirred for 10 h at room temperature followed by dilution with hexane (20 mL) and washing with brine. The organic extracts were dried over MgSO$_4$, filtered, and concentrated. The crude product was purified by distillation under vacuum to give a colorless oil as product (3.4 g, 58% yield). ^{1}H NMR (CDCl$_3$, 500 MHz, TMS): δ 1.94 (6H, s), 5.27 (2H, d, J = 10.0 Hz), 5.38 (2H, d, J = 15.0 Hz), 5.70−5.73 (1H, m), 5.82−5.89 (2H, m). ^{13}C NMR (CDCl$_3$, 125 MHz, TMS): 30.7, 55.8, 76.4, 117.8, 134.3, 170.5. MS (ESI) calcd for $C_9H_{13}BrO_2Na$: $[M + Na]^+$ 255.00; found: 254.85.

Synthesis of Macroinitiator (PE-OH)$_2$-Br. A typical polyhomologation procedure is as follows. To a solution of 1,4-pentadiene-3-yl 2-bromo-2-methylpropanoate (0.23 g, 1.0 mmol) in THF (4.0 mL) a freshly prepared thexylborane (0.50 mL, ∼0.73 M) was added dropwise at 0 °C under Ar, and the mixture was kept under stirring for 4 h at room temperature to give the organoborane solution.

A 100 mL Schlenk flask, charged with methylide solution (10 mL, 1.7 M in toluene) and toluene (20 mL), was heated to 60 °C with stirring under Ar. Then 2.0 mL of the above prepared organoborane solution was added. After stirring at 60 °C for 10 min, 0.10 mL of the reaction solution was taken out and added to water containing phenolphthalein. A neutral solution (pH indicator) indicated the complete consumption of the ylide. Then TAO·2H$_2$O (0.40 g) was added, and the mixture was kept under stirring at 80 °C for 4 h. The mixture was poured into cold methanol (300 mL), and the white solids were filtered, dried under vacuum, and characterized by ^{1}H NMR and HT-GPC [(PE$_{546}$-OH)$_2$-Br, $M_{n,NMR} = 15.5 \times 10^3$, PDI = 1.29].

Synthesis of Functionalized 3-Miktoarm Star Copolymer (PE-OH)$_2$-(PS-Br). A typical ATRP procedure is as follows. CuBr (2.6 mg, 0.018 mmol), styrene (0.45 mL, 3.9 mmol), and toluene (5.0 mL) were placed into a 100 mL Schlenk flask. The mixture was subjected to two freeze−pump−thaw cycles, and then PMDETA (8.0 μL, 0.036 mmol) was added and the mixture was kept stirring at room temperature for 20 min under Ar. Then the macroinitiator (PE$_{546}$-OH)$_2$-Br (0.20 g, 0.013 mmol) was added, and the mixture was subjected to another two freeze−pump−thaw cycles. The solution was immediately immersed into an oil bath set at 100 °C to start the polymerization under stirring. After 24 h, the polymerization was stopped by cooling in a liquid nitrogen bath. The reaction mixture was poured into cold methanol (300 mL) with stirring. The polymer was filtered, washed with methanol, dried under vacuum, and characterized by ^{1}H NMR and HT-GPC ($M_{n,NMR} = 19.3 \times 10^3$, PDI = 1.30).

Synthesis of 3-Miktoarm Star Copolymer (PE-*b*-PS-Br)$_2$-(PS-Br). A typical esterification and ATRP procedure are given below for the synthesis of (PE$_{568}$-*b*-PS$_{57}$-Br)$_2$-(PS$_{57}$-Br), as an example. (PE$_{568}$-OH)$_2$-Br (0.20 g, 0.024 mmol of OH) and toluene (20 mL) were placed into a 100 mL Schlenk flask, and the mixture was kept under stirring vigorously at 100 °C under Ar. Pyridine (0.10 mL, 1.2 mmol) was added followed by 2-bromo-2-methylpropionyl bromide (0.12 mL, 1.0 mmol), and stirring for 10 h. The reaction mixture was cooled to room temperature and poured into 300 mL of acidic methanol (containing 30 mL of 1 M aqueous HCl). The polymer was filtered, washed successively with methanol (2 × 20 mL), 1 M aqueous HCl (2 × 10 mL), and methanol (2 × 20 mL), and dried at 50 °C for 3 h in vacuum to give an off-white solid (PE$_{568}$-Br)$_2$-Br (0.19 g, 90% yield).

ATRP of styrene (0.63 mL, 5.4 mmol) catalyzed by CuBr (5.5 mg, 0.038 mmol)/PMDETA (16 μL, 0.076 mmol) and initiated by (PE$_{568}$-Br)$_2$-Br (0.15 g, 0.018 mmol of Br) in toluene (5.0 mL) at 100 °C gave the polymer (PE$_{568}$-*b*-PS$_{57}$-Br)$_2$-(PS$_{57}$-Br) ($M_{n,NMR} = 34.2 \times 10^3$, PDI = 1.35). More details on the ATRP procedure are given above.

Synthesis of 3-Miktoarm Star Terpolymer (PE-*b*-PMMA-Br)$_2$-(PS-*b*-PMMA-Br). As an example the synthesis of (PE$_{360}$-*b*-PMMA$_{83}$-Br)$_2$-(PS$_{60}$-*b*-PMMA$_{83}$-Br) is given. (PE$_{360}$-OH)$_2$-(PS$_{60}$-Br) (80 mg, 0.010 mmol of OH) was converted to (PE$_{360}$-Br)$_2$-(PS$_{60}$-Br) (47 mg, 58% yield) by reaction with 2-bromo-2-methylpropionyl bromide (0.12 mL, 1.0 mmol) in the presence of pyridine (0.10 mL, 1.2 mmol) in toluene (5 mL) at 100 °C.

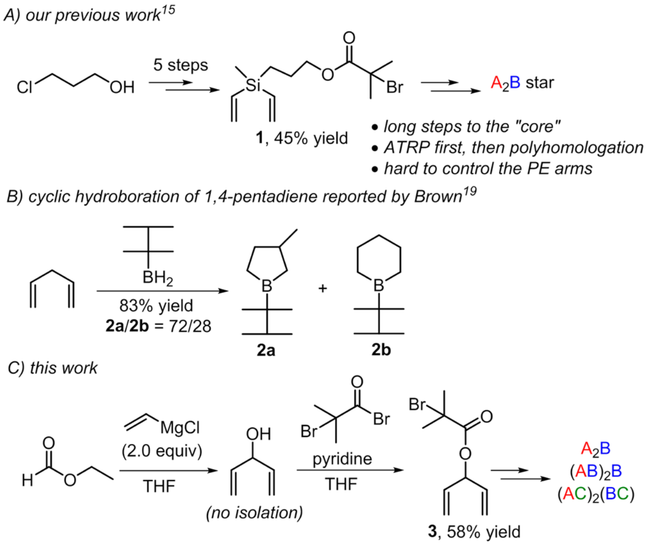
ATRP of MMA (0.55 mL, 5.2 mmol) catalyzed by CuBr (1.7 mg, 0.012 mmol)/PMDETA (5.0 uL, 0.024 mmol) and initiated by (PE$_{360}$-Br)$_2$-(PS$_{60}$-Br) (47 mg, 0.0085 mmol of Br) in toluene (5.0 mL) at 100

°C gave the polymer $(PE_{360}\text{-}b\text{-}PMMA_{83}\text{-}Br)_2\text{-}(PS_{60}\text{-}b\text{-}PMMA_{83}\text{-}Br)$ ($M_{n,NMR}$ = 41.4 × 10^3, PDI = 1.41). More details on the ATRP procedure are given above.

■ RESULTS AND DISCUSSION

Synthesis of PE-Based Macroinitiator $(PE\text{-}OH)_2\text{-}Br$. In our previous work,[15] the heterofunctional initiator 3-(methyldivinylsilyl)propyl 2-bromo-2-methylpropanoate, synthesized from 3-chloro-1-propanol in five steps, was used followed by cyclic hydroboration, ATRP, and polyhomologation to afford the PE_2-PS 3-miktoarm star copolymers (Scheme 1A).

Scheme 1. (A) Previous Work: Laborious Synthesis Route for A_2B Miktoarm Star; (B) Cyclic Hydroboration of 1,4-Pentadiene with Thexylborane; (C) This Work: Facile Synthesis of A_2B, $(AB)_2B$, and $(AC)_2(BC)$ 3-Miktoarm Stars Starting from Ethyl Formate

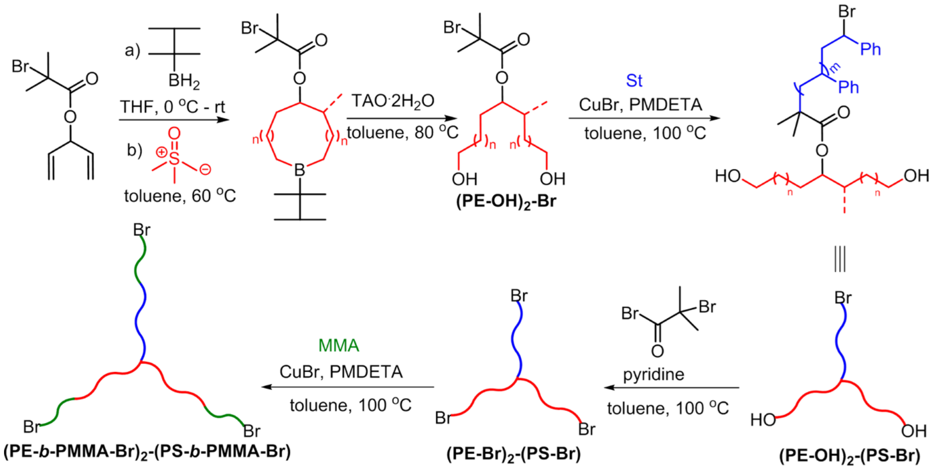


Considering the laborious and time-consuming synthesis of the previous heterofunctional initiator, the following facile synthetic route was developed. 1,4-Pentadien-3-ol was first prepared by reaction of vinylmagnesium chloride with ethyl formate, and without purification it was converted to the heterofunctional initiator (58% yield, two steps) by esterification with 2-bromoisobutyryl bromide (Scheme 1C). Hydroboration of 1,4-pentadiene moiety with thexylborane gave a mixture of five- and six-membered boracyclanes (**2a** and **2b**, Scheme 1B)[19] exactly as in the case of methylphenyldivinylsilane.[15]

The 1,4-pentadiene group of the new initiator 1,4-pentadiene-3-yl 2-bromo-2-methylpropanoate, after transformation to B-thexylboracycles, was used to initiate the polyhomologation and the 2-bromo-2-methylpropanoate group the ATRP. In our previous work when first ATRP and then polyhomologation were performed, the molecular weight of the obtained miktoarm star copolymers was much higher than expected.[15] This discrepancy was attributed on one hand to the poor efficiency of the PS-macroinitiator for polyhomologation and on the other hand to the unknown concentration of boron macroinitiator, as a consequence of accidental oxidation before polyhomologation. Hence, we decided to start with the polyhomologation followed by ATRP (Scheme 2). To make sure the whole thexylborane will be consumed, since unreacted (initiator of polyhomologation) will contaminate the miktoarm star with linear PE, excess of 1,4-pentadiene-3-yl 2-bromo-2-methylpropanoate was used. The resultant organoborane solution was added to the preheated ylide solution (60 °C); the mixture became neutral in 10 min, indicating that the ylide was rapidly and quantitatively consumed. After the oxidation/hydrolysis with trimethylamine *N*-oxide dihydrate ($TAO{\cdot}2H_2O$), a bromo-functionalized *α*,*ω*-dihydroxyl polyethylene $(PE{-}OH)_2\text{-}Br$ was obtained. Seven samples with different molecular weights were synthesized (Table 1). The molecular weights were determined by ^1H NMR end group analysis ($M_{n,NMR}$ = (3.3−32.9) × 10^3, Figure 1) and the polydispersities by high temperature gel permeation chromatography (HT-GPC) with polystyrene standards (M_w/M_n = 1.28−1.59). Increasing the reaction temperature from 60 to 80 °C did not improve the polydispersity (Table 1, entries 1 and 2). The high polydispersity (1.59) but still monomodal (Figure 2A, green) of the highest molecular weight PE (32.9 × 10^3, Table 1, entry 7) is probably due to its insolubility (heterogeneous polymerization).

Since boranes are very sensitive to air, the amount of the initiator is less than that calculated from thexylborane; consequently, the molecular weight of the PE produced is higher than expected. To exactly control the molecular weight of

Scheme 2. Synthesis Routes toward A_2B 3-Miktoarm Star Copolymers $(PE\text{-}OH)_2\text{-}(PS\text{-}Br)$ and $(AC)_2(BC)$ Star Terpolymers $(PE\text{-}b\text{-}PMMA\text{-}Br)_2\text{-}(PS\text{-}b\text{-}PMMA\text{-}Br)$



the PE, the real concentration of the organoborane solution should be determined. For this purpose, $(PE_{546}\text{-}OH)_2\text{-}Br$ ($M_{n,NMR}$ = 15.5 × 10^3, PDI = 1.29) was synthesized first (Table 1, entry 6), and the number-average degree of polymerization of PM (one chain) was calculated to be ($M_{n,NMR}$ − 233)/14/2 = 546 (233 is the molecular weight of the diene initiator, 14 of the $-CH_2-$ repeating unit, two chains). Consequently, the actual concentration of organoborane is 17 mmol/(546 × 2 × 2.0 mL) = 0.0078 mmol/mL (17 is the amount of dimethylsulfoxonium methylide in mmol, 10 mL corresponds to 1.7 mmol/mL, see Experimental Section; 2.0 mL is the volume of organoborane solution; two chains). Using this actual concentration, a new $(PE_{1168}\text{-}OH)_2\text{-}Br$, with controlled molecular weight as shown by comparison of theoretical and determined molecular weight ($M_{n,theor}$ = 29.9 × 10^3, $M_{n,NMR}$ = 32.9 × 10^3, PDI = 1.59) (Table 1, entry 7) was synthesized.

The proof of the successful synthesis of $(PE\text{-}OH)_2\text{-}Br$ was derived from ^1H NMR and GPC results. As shown in Figures 1A and 1B, the characteristic chemical shifts of vinyl protons in 1,4-pentadiene-3-yl 2-bromo-2-methylpropanoate at δ = 5.9−5.8

Table 1. Molecular Characteristics of $(PE\text{-}OH)_2\text{-}Br$

entry	sample	$M_{n,theor}$ × 10^{-3}	$M_{n,NMR}$ × 10^{-3} [a]	DP (PM)[a]	$M_{n,GPC}$ × 10^{-3} [b]	PDI[b]
1	$(PE_{110}\text{-}OH)_2\text{-}Br$	–[c]	3.3	110	4.1	1.34
2[d]	$(PE_{113}\text{-}OH)_2\text{-}Br$	–[c]	3.4	113	3.4	1.37
3	$(PE_{360}\text{-}OH)_2\text{-}Br$	–[c]	10.3	360	17.4	1.38
4	$(PE_{185}\text{-}OH)_2\text{-}Br$	–[e]	5.4	185	7.5	1.28
5	$(PE_{568}\text{-}OH)_2\text{-}Br$	14.7	16.4	568	28.7	1.36
6	$(PE_{546}\text{-}OH)_2\text{-}Br$	–[e]	15.5	546	18.4	1.29
7[f]	$(PE_{1168}\text{-}OH)_2\text{-}Br$	29.9	32.9	1168	44.0	1.59

[a] $M_{n,NMR}$ and DP [degree of polymerization of one polymethylene (PM) chain] were calculated from ^1H NMR spectrum (toluene-d_8) using the area ratio of protons in terminal CH_2OH at δ = ~3.5 ppm to the ones on the backbone. [b] $M_{n,GPC}$, PDI = M_w/M_n, determined by HT-GPC (1,2,4-trichlorobenzene, 150 °C, PS standards). [c] Not measured. [d] Polyhomologation reaction was performed at 80 °C. [e] Sample synthesized for determining the real concentration of organoborane initiator. [f] $M_{w,GPC\text{-}LS}$ = 47.2 × 10^3, $PDI_{GPC\text{-}LS}$ = 1.34, determined by triple-detection HT-GPC; see Supporting Information.

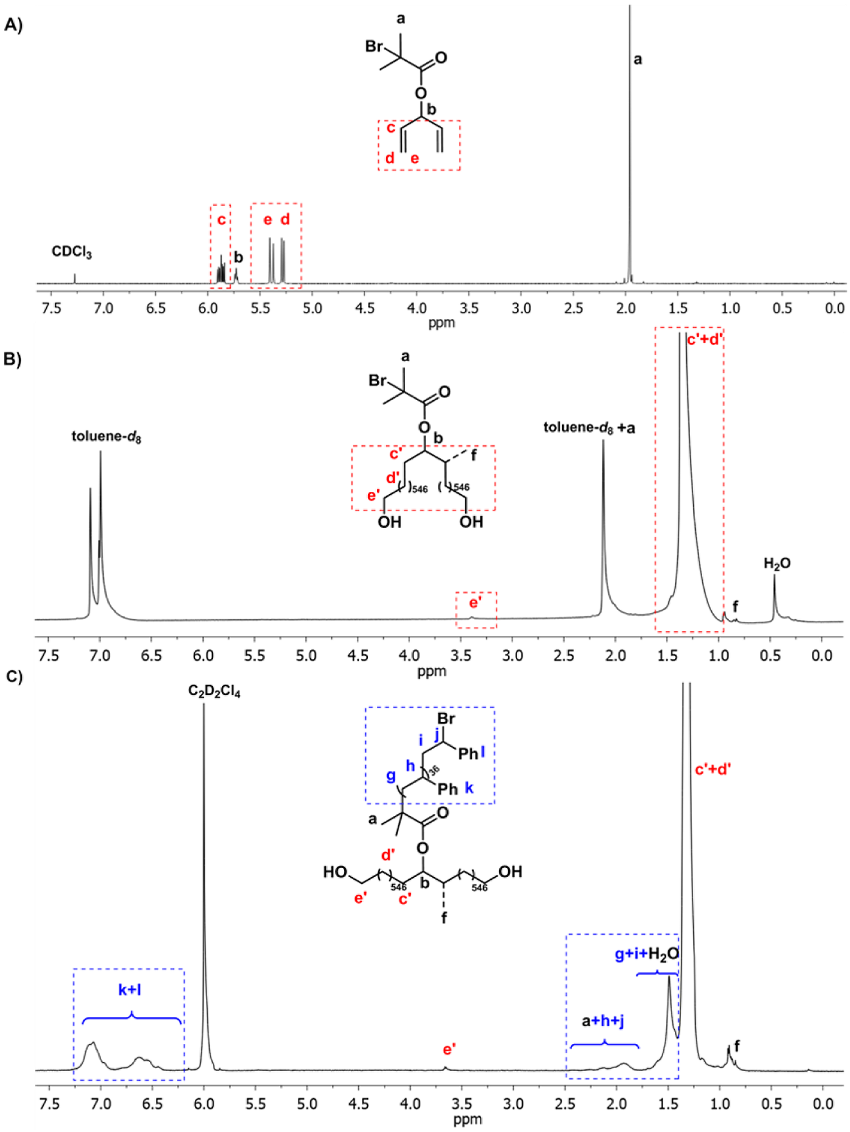


Figure 1. NMR spectra of (A) 1,4-pentadiene-3-yl 2-bromo-2-methylpropanoate in chloroform-*d*. (B) $(PE_{546}\text{-}OH)_2\text{-}Br$ in toluene-d_8 at 90 °C. (C) $(PE_{546}\text{-}OH)_2\text{-}(PS_{37}\text{-}Br)$ in 1,1,2,2-tetrachloroethane-d_2 at 90 °C.

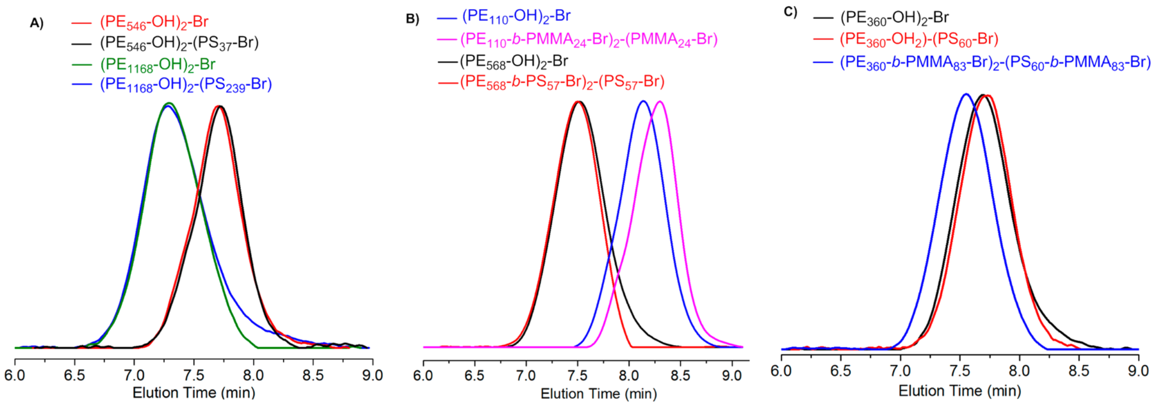


Figure 2. GPC chromatograms of linear PEs and the corresponding miktoarm star polymers.

Table 2. ATRP Reaction Conditions and Molecular Characteristics of A_2B, $(AB)_2B$, and $(AC)_2(BC)$ Stars

star co/terpolymer	macroinitiator	M[a]	[M]/[Br][b]	$M_{n,NMR}$[c] × 10^{-3}	$M_{n,GPC}$[d] × 10^{-3}	PDI[d]	PE[c] (wt %)
$(PE_{113}\text{-}OH)_2\text{-}(PS_{22}\text{-}Br)$	$(PE_{113}\text{-}OH)_2\text{-}Br$	St	300/1	5.7	2.7	1.29	60
$(PE_{360}\text{-}OH)_2\text{-}(PS_{60}\text{-}Br)$	$(PE_{360}\text{-}OH)_2\text{-}Br$	St	260/1	16.5	16.8	1.30	62
$(PE_{546}\text{-}OH)_2\text{-}(PS_{37}\text{-}Br)$	$(PE_{546}\text{-}OH)_2\text{-}Br$	St	600/1	19.3	17.5	1.30	80
$(PE_{1168}\text{-}OH)_2\text{-}(PS_{239}\text{-}Br)$[e]	$(PE_{1168}\text{-}OH)_2\text{-}Br$	St	600/1	57.8	45.0	1.49	57
$(PE_{110}\text{-}b\text{-}PMMA_{24}\text{-}Br)_2\text{-}(PMMA_{24}\text{-}Br)$	$(PE_{110}\text{-}Br)_2\text{-}Br$	MMA	200/1	10.5	5.4	1.40	30
$(PE_{568}\text{-}b\text{-}PS_{57}\text{-}Br)_2\text{-}(PS_{57}\text{-}Br)$	$(PE_{568}\text{-}Br)_2\text{-}Br$	St	300/1	34.2	31.3	1.35	48
$(PE_{360}\text{-}b\text{-}PMMA_{83}\text{-}Br)_2\text{-}(PS_{60}\text{-}b\text{-}PMMA_{83}\text{-}Br)$	$(PE_{360}\text{-}Br)_2\text{-}(PS_{60}\text{-}Br)$	MMA	600/1	41.4	25.5	1.41	24

[a] M: monomer. [b] The reaction was performed in toluene at 100 °C for 24 h and [Br]/[CuBr]/[PMDETA] = 1:1.4:2.8. [c] $M_{n,NMR}$ and PE content were calculated from ^1H NMR spectra (toluene-d_8 or 1,1,2,2-tetrachloroethane-d_2, 80 or 90 °C). [d] $M_{n,GPC}$, PDI = M_w/M_n, determined by HT-GPC (1,2,4-trichlorobenzene, 150 °C, PS standards). [e] $M_{w,GPC\text{-}LS}$ = 67.2 × 10^3, $PDI_{GPC\text{-}LS}$ = 1.30, determined by triple-detection HT-GPC; see Supporting Information.

ppm (m, H_c), δ = 5.4 ppm (d, H_e), and δ = 5.3 ppm (d, H_d) disappeared after hydroboration/polyhomologation/oxidation/hydrolysis reaction, and a new peak at δ = 3.4 ppm for the $-CH_2-$ connected to hydroxy group ($H_{e'}$) appeared, indicating that the polymerization initiated from both initiating sites. The observed integration area ratio of the aliphatic protons at δ = 1.1−1.5 ppm ($H_{c'\&d'}$, two protons for each methylene unit, two PE chains) [$S_{c'\&d'}$/4H] to that of protons assigned to $-CH_2-$ connected to hydroxyl group at δ = 3.4 ppm ($H_{e'}$, two protons for each PE arm, two end groups) [$S_{e'}$/4H] was derived from the following formula: $n = (S_{c'\&d'}/4H):(S_{e'}/4H)$, which is the degree of polymerization of each PE chain. This integrated ratio was used to determine the number-average molecular weight of the macroinitiator $(PE\text{-}OH)_2\text{-}Br$, $M_{n,NMR} = (S_{c'\&d'}/S_{e'}) \times MW_{CH2}$ (14) × 2 + $MW_{initiator}$ (233). The B-thexyl site was inactive to polyhomologation since only one peak appeared in the GPC traces (Figure 2A, red and green).

Synthesis of A_2B Star Copolymers. To synthesize A_2B miktoarm star copolymers, ATRP was carried out using $(PE\text{-}OH)_2\text{-}Br$ as macroinitiator. For example, the ATRP of styrene was performed with $(PE_{546}\text{-}OH)_2\text{-}Br$ as macroinitiator and copper(I) bromide (CuBr)/*N*,*N*,*N*′,*N*′,*N*″,*N*″-pentamethyldiethylenetriamine (PMDETA) as catalyst/ligand in toluene. High temperature (100 °C) was needed since linear PE possesses poor solubility at lower temperatures. The ratio [St]/[Br] was 600; the reaction was terminated after 24 h, followed by precipitation in methanol to give the polymer. The fingerprints for PS and PE blocks are evident in the ^1H NMR spectrum (1,1,2,2-tetrachloroethane-d_2, 90 °C) (Figure 1C). The observed integration area ratio of the aromatic protons at δ = 6.4−7.3 ppm ($H_{k\&l}$, five protons for each St unit) [$S_{k\&l}$/5H] to that of protons assigned to the $-CH_2-$ connected to hydroxyl group at δ = 3.7 ppm ($H_{e'}$, two protons for each PE arm, total two PE arms) [$S_{e'}$/4H] was derived from the following formula: $m = (S_{k\&l}/5H):(S_{e'}/4H) = 37$, which is the degree of polymerization of PS chain. The integration area ratio of aliphatic protons at δ = 1.0−1.4 ppm ($H_{c'\&d'}$, two protons for each methylene unit, two PE arms) [$S_{c'\&d'}$/4H] to that of end group's protons [$S_{e'}$/4H] was derived from the same formula as above: $n = (S_{c'\&d'}/4H):(S_{e'}/4H) = 660$, which is the degree of polymerization of one PE arm. Considering that the peaks of $H_{g,i\&H_2O}$ were close to the peaks of $H_{c'\&d'}$, the integration of protons [$S_{c'\&d'}$] was not so accurate giving n = 546 instead of the above calculated value 660. This indicates that ATRP initiated by $(PE_{546}\text{-}OH)_2\text{-}Br$ although the protons of $H_{a\&b}$ were not identifiable in ^1H NMR spectra. The number-average molecular weight of the A_2B star $(PE_{546}\text{-}OH)_2\text{-}(PS_{37}\text{-}Br)$ is $M_{n,NMR} = m\ (37) \times MW_{St}(104) + n\ (546) \times MW_{CH2}$ (14) × 2 + $MW_{initiator}$ (233) = 19.3 × 10^3.

Four A_2B star samples were synthesized, and the corresponding molecular characteristics are shown in Table 2. The GPC curves in Figure 2A show the variation of molecular weights and molecular weight distributions of the star polymers prepared from the linear PE macroinitiators. A slight shift of the elution peak of star polymer $(PE_{546}\text{-}OH)_2\text{-}(PS_{37}\text{-}Br)$ to the lower molecular weight side, as compared to the linear PE macroinitiator $(PE_{546}\text{-}OH)_2\text{-}Br$, was observed. In the case of $(PE_{1168}\text{-}OH)_2\text{-}(PS_{239}\text{-}Br)$, a shift to slightly higher molecular weight side occurred, compared with the corresponding linear one. This can be attributed to the branched structure of the star polymer compared to the linear one.[21] Separation of macromolecules by GPC is based on the size or more specifically the hydrodynamic radius (R_h). To compare the size of the linear and star polymers $(PE_{11686}\text{-}OH)_2\text{-}Br$ and $(PE_{1168}\text{-}OH)_2\text{-}(PS_{239}\text{-}Br)$ were characterized by HT-GPC equipped with refractive index (RI), light

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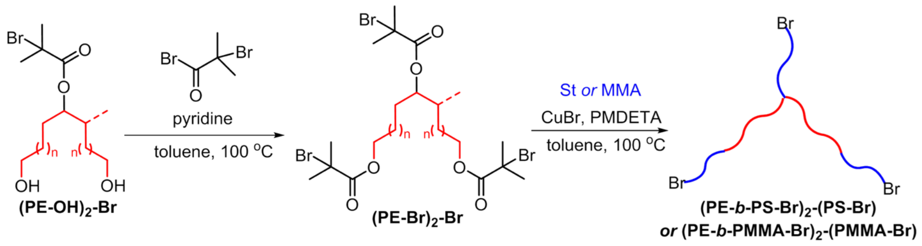
Scheme 3. Synthesis Routes toward $(AB)_2B$ Star Copolymers $(PE\text{-}b\text{-}PS\text{-}Br)_2\text{-}(PS\text{-}Br)$ and $(PE\text{-}b\text{-}PMMA\text{-}Br)_2\text{-}(PMMA\text{-}Br)$



scattering (LS), and viscometry detectors. The calculated R_h of the linear PE was 6.9 nm, and the branched polymer was 7.6 nm. Considering the molecular weight of the star copolymer ($M_{w,GPC\text{-}LS}$ = 67.2 × 10^3, $PDI_{GPC\text{-}LS}$ = 1.30) increased largely compared to that of the linear one ($M_{w,GPC\text{-}LS}$ = 47.2 × 10^3, $PDI_{GPC\text{-}LS}$ = 1.34), the R_h of the star copolymer increased slightly, which is in accordance with the tiny shift of the elution peak from 13.85 to 13.81 mL (RI peak, see Figure S1, Supporting Information).

Synthesis of $(AB)_2B$ Star Copolymers. To synthesize $(AB)_2B$ star copolymers, a macroinitiator with three ATRP initiating sites was prepared from $(PE\text{-}OH)_2\text{-}Br$ by esterification of the two hydroxyl groups with 2-bromoisobutyryl bromide at 100 °C in toluene (Scheme 3). As shown in Figure 3A, the characteristic chemical shift due to the protons connected with the hydroxyl groups in $(PE_{568}\text{-}OH)_2\text{-}Br$ at δ = 3.4 ppm (H_e) disappeared after esterification, and a new peak at δ = 4.0 ppm of the $-CH_2-$ connected to ester group ($H_{e'}$) appeared, indicating the complete formation of $(PE_{568}\text{-}Br)_2\text{-}Br$. Then ATRP of styrene initiated by the resultant $(PE_{568}\text{-}Br)_2\text{-}Br$ with CuBr/PMDETA as catalyst/ligand at 100 °C in toluene was performed. After 24 h, the polymer was precipitated in methanol and dried under vacuum. By the same method, $(PE_{110}\text{-}Br)_2\text{-}Br$ was synthesized and used as macroinitiator for the ATRP of MMA. The ATRP reaction conditions and the characteristics of the two $(AB)_2B$ star copolymers are shown in Table 2.

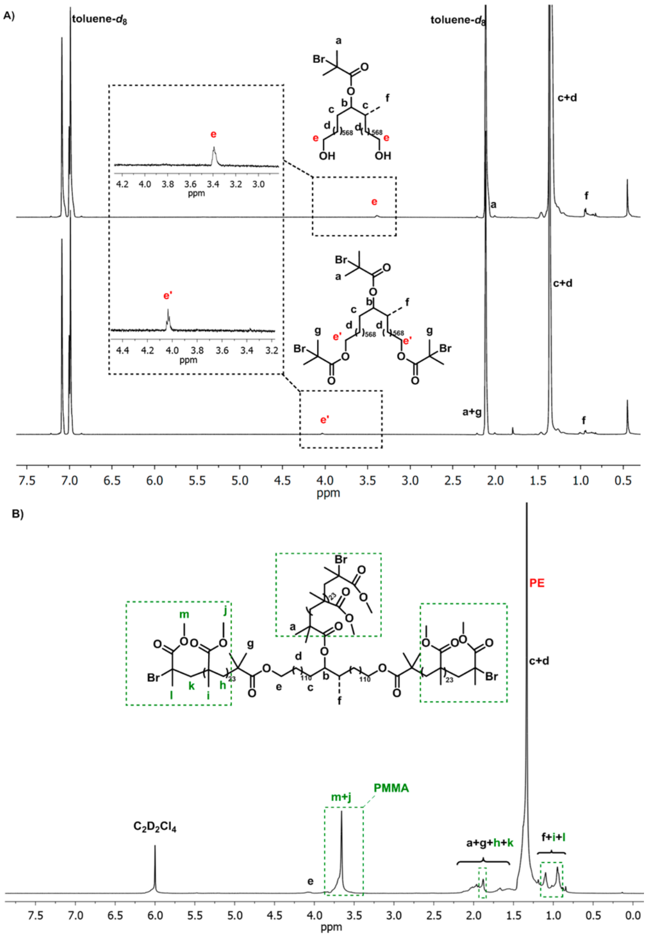


Figure 3. NMR spectra of (A) $(PE_{568}\text{-}OH)_2\text{-}Br$ and $(PE_{568}\text{-}Br)_2\text{-}Br$ in toluene-d_8 at 90 °C and (B) $(PE_{110}\text{-}b\text{-}PMMA_{24}\text{-}Br)_2\text{-}(PMMA_{24}\text{-}Br)$ in 1,1,2,2-tetrachloroethane-d_2 at 90 °C.

As shown in Figure 3B and Figure S2, the fingerprints of PMMA and PS segments are clearly found in the synthesized $(AB)_2B$ star copolymers. By comparison of the integration of the relevant peaks, the degrees of polymerization of the PS and PMMA segments were calculated [$(PE_{568}\text{-}b\text{-}PS_{57}\text{-}Br)_2\text{-}(PS_{57}\text{-}Br)$ and $(PE_{110}\text{-}b\text{-}PMMA_{24}\text{-}Br)_2\text{-}(PMMA_{24}\text{-}Br)$, see Supporting Information]. The evolution of molecular weight for $(AB)_2B$ star copolymers was investigated by HT-GPC. As shown in Figure 2B, the elution peak of $(PE_{110}\text{-}b\text{-}PMMA_{24}\text{-}Br)_2\text{-}(PMMA_{24}\text{-}Br)$ shifted to a lower molecular weight side, and the elution peak of $(PE_{568}\text{-}b\text{-}PS_{57}\text{-}Br)_2\text{-}(PS_{57}\text{-}Br)$ shifted to a slightly higher molecular weight side, when compared with the peak of the corresponding linear PE. The polydispersity index was relatively low ($M_w/M_n \leq 1.4$) and the trace monomodal, suggesting that the arm growing step was well-controlled, indicating the high efficiency of the ATRP macroinitiator.

Synthesis of $(AC)_2(BC)$ Star Terpolymers. To synthesize $(AC)_2(BC)$ star terpolymers, the two terminal hydroxyl groups of A_2B star copolymer $(PE_{360}\text{-}OH)_2\text{-}(PS_{60}\text{-}Br)$ were reacted with 2-bromoisobutyryl bromide at 100 °C in toluene to give $(PE_{360}\text{-}Br)_2\text{-}(PS_{60}\text{-}Br)$ containing three initiating sites for ATRP (Scheme 2). As shown in the ^1H NMR spectrum (Figure S3), the characteristic chemical shift due to protons connected with hydroxyl group in $(PE_{360}\text{-}OH)_2\text{-}(PS_{60}\text{-}Br)$ at δ = 3.7 ppm disappeared after esterification, and a new peak at δ = 4.0 ppm of the $-CH_2-$ connected to ester group appeared, indicating the completely conversion of the −OH to −Br. Then the ATRP of MMA initiated by the synthesized $(PE_{360}\text{-}Br)_2\text{-}(PS_{60}\text{-}Br)$ with CuBr/PMDETA as catalyst/ligand at 100 °C in toluene was performed, and the obtained polymer was characterized by ^1H NMR and HT-GPC. The fingerprints of the PMMA segment were evident in the ^1H NMR spectrum (Figure S3): the signals of $CH_3-C{=}O$ protons at 3.7 ppm, $-CH_2-C-$ at 1.9 ppm, and CH_3-C- at 1.1 and 0.9 ppm. The degree of polymerization of the PMMA segment was calculated by comparison of the integration of the relevant peaks [$(PE_{360}\text{-}b\text{-}PMMA_{83}\text{-}Br)_2\text{-}(PS_{60}\text{-}b\text{-}PMMA_{83}\text{-}Br)$, see Supporting Information]. The esterification reaction and the PMMA chains were also confirmed by FT-IR spectroscopy (Figure S4). The characteristic ester carbonyl absorbance peak at ~1729 cm^{-1} increased, in accordance with the increase amount of ester carbonyl groups in the polymer. The

GPC curves in Figure 3C show that the elution peak of $(PE_{360}\text{-}b\text{-}PMMA_{83}\text{-}Br)_2\text{-}(PS_{60}\text{-}b\text{-}PMMA_{83}\text{-}Br)$ shifted to higher molecular weight than that of $(PE_{360}\text{-}OH)_2\text{-}(PS_{60}\text{-}Br)$. All peaks are monomodal/symmetric and the polydispersity of final star terpolymer low (M_w/M_n = 1.41, Table 2), indicating the chain extension polymerization from A_2B to $(AC)_2(BC)$ star polymer was highly efficient.

DSC Analysis of Linear PEs and PE-Based Star Co/Terpolymers. The DSC traces for the linear PEs and the corresponding 3-miktoarm star co/terpolymers are shown in Figure 4 and Figure S5. The linear PEs with M_n 3300−32.9 × 10^3 exhibit melting temperatures (T_m) 117.3−128.4 °C and crystallinities 56.9−65.7%. In the case of the A_2B star copolymers $(PE\text{-}OH)_2\text{-}(PS\text{-}Br)$, the T_m does not change appreciably even when the content of PE block is as low as 48 wt % [$(PE_{568}\text{-}b\text{-}PS_{57}\text{-}Br)_2\text{-}(PS_{57}\text{-}Br)$]. It seems that the crystallization of the PE block is hindered by the covalently attached glassy PS block,[22] leading to lower values 58.2−31.1%; the higher the PS content, the lower the crystallinity. This is much more pronounced in the case of $(AB)_2B$ star copolymer $(PE_{110}\text{-}b\text{-}PMMA_{24}\text{-}Br)_2\text{-}(PMMA_{24}\text{-}Br)$, 25.4%, and of $(AC)_2(BC)$ star terpolymer $(PE_{360}\text{-}b\text{-}PMMA_{83}\text{-}Br)_2\text{-}(PS_{60}\text{-}b\text{-}PMMA_{83}\text{-}Br)$, 18.9%. In the case of $(PE_{110}\text{-}b\text{-}PMMA_{24}\text{-}Br)_2\text{-}(PMMA_{24}\text{-}Br)$ (113.3 °C) and $(PE_{360}\text{-}b\text{-}PMMA_{83}\text{-}Br)_2\text{-}(PS_{60}\text{-}b\text{-}PMMA_{83}\text{-}Br)$ (123 °C) the T_m is lower than the corresponding PE homopolymer (119.6 and 128.2 °C, respectively) probably attributed to the reduced PE chain mobility imposed by the PMMA chains.[23] Obviously the T_g of PS and PMMA are obscured by the melting traces of PE.

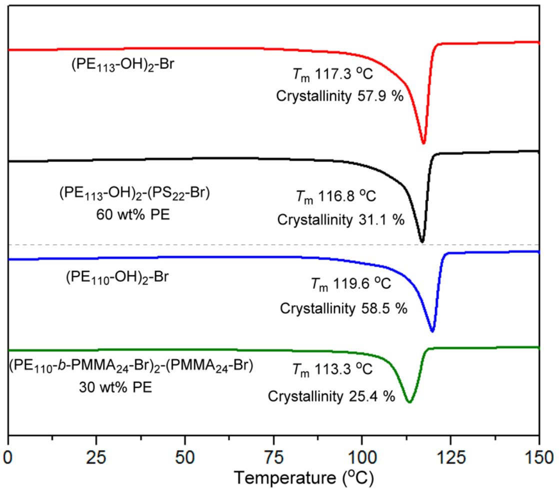


Figure 4. DSC traces for $(PE_{113}\text{-}OH)_2\text{-}Br$, $(PE_{113}\text{-}OH)_2\text{-}(PS_{22}\text{-}Br)$, $(PE_{110}\text{-}OH)_2\text{-}Br$, and $(PE_{110}\text{-}b\text{-}PMMA_{24}\text{-}Br)_2\text{-}(PMMA_{24}\text{-}Br)$.

■ CONCLUSION

A "core-first" synthetic strategy toward well-defined PE-based miktoarm star co/terpolymers was developed by using the facile synthesized 1,4-pentadiene-3-yl 2-bromo-2-methylpropanoate-ATRP initiator/precursor for polyhomologation initiator. Hydroboration of the diene group with thexylborane followed by polyhomologation of dimethylsulfoxonium methylide leads to α,ω-dihydroxylpolyethylene with Br-initiating ATRP sites employed to synthesize A_2B, $(AB)_2B$, and $(AC)_2(BC)$ 3-miktoarm star co/terpolymers. In all synthesized star polymers, the crystallinity decreased due to the reduced PE chain mobility imposed by the other heteroblocks. This general strategy opens new horizons toward PE-based complex macromolecular architectures when combining with other living and living/controlled polymerization techniques, such as ring-opening polymerization (ROP), nitroxide-mediated polymerization (NMP), and reversible addition−fragmentation chain transfer (RAFT).

■ ASSOCIATED CONTENT

Ⓢ Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acs.macromol.6b00291.

Figures S1−S5 (PDF)

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Notes

The authors declare no competing financial interest.

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