Synthesis of Block Copolymers of Ethylene with Styrene and *n*-Butyl Acrylate via a Tandem Strategy Combining Ethylene "Living" Polymerization Catalyzed by a Functionalized Pd−Diimine Catalyst with Atom Transfer Radical Polymerization

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ABSTRACT: We report a new two-step tandem strategy combining two versatile "living" polymerization techniques, Pd−diimine catalyzed ethylene "living" polymerization and atom transfer radical polymerization (ATRP), for the synthesis of functionalized polyethylene (PE) diblock copolymers containing an ethylene block and a functional monomer block, such as styrene and *n*-butyl acrylate. The key to the success of this tandem strategy is the development of a novel functionalized Pd−diimine catalyst, $[(ArN{=}C(Me){-}(Me)C{=}NAr)Pd(CH_2)_3C(O)O(CH_2)_2OC(O)C(CH_3)_2Br]^+SbF_6^-$ (Ar = 2,6-(iPr)$_2$C$_6$H$_3$) (**3**), which uniquely contains a 2-bromoisobutyryl substituting group on its chelate structure. This catalyst was synthesized by convenient equimolar reaction of the acetonitrile Pd−diimine adduct, $[(ArN{=}C(Me){-}(Me)C{=}NAr)Pd(CH_3)(N{\equiv}CMe)]^+SbF_6^-$ (Ar = 2,6-(iPr)$_2$C$_6$H$_3$) (**1**), with a functional acrylate monomer, 2-(2-bromoisobutyryloxy) ethyl acrylate (BIEA). The remarkable feature of **3** lies in its unprecedented ability to catalyze ethylene "living" polymerization that directly gives rise to telechelic PE chains bearing an end-capping 2-bromoisobutyryl group active for initiating ATRP. The resulting end-functionalized PEs can thus be directly used as macroinitiators to subsequently initiate ATRP of functional monomers, like styrene and *n*-butyl acrylate used in this work, in the second step of this tandem strategy to synthesize functionalized diblock copolymers. Because of the "living" polymerization nature of both steps in this tandem strategy, we demonstrate that the functionalized block copolymers synthesized possess well-defined structures with narrow molecular weight distributions and controllable lengths for both PE and functional monomer blocks.

Introduction

Developing functionalized polyolefins is an important and challenging theme in research and development of polyolefins. The presence of functional groups on the nonpolar polyolefin chains imparts functionalized polyolefins with some enhanced materials properties, such as toughness, barrier properties, surface properties, miscibility with other polar polymers, etc.[1,2] One recent interest in this area is to develop functionalized polyolefin block copolymers containing covalently connected polyolefin and functional polymer blocks (such as polystyrene, polyacrylates, etc.). The constituting polymer blocks in such copolymers are generally thermodynamically incompatible, thus giving rise to materials with a variety of bulk microstructures and consequently, with various important applications such as thermoplastic elastomers, compatabilizers, and high-impact plastics.[2,3]

Synthesis of functionalized polyolefin block copolymers is somehow very difficult. The traditional sequential "living" polymerization method using Ziegler−Natta and metallocene catalysts have very limited use due to the sensitivity of most early transition metal catalysts toward polar functional groups.[4] Moreover, different polymerization mechanisms are often required for polymerization of mechanistically incompatible monomers in the block copolymers, which further diminishes the possibility of finding a suitable metal catalyst.[4] To date, organolanthanide complexes,[5] LnRCp$^*_2$ (Ln = Sm, Yb, Lu; R = H, CH$_3$), and the V(acac)$_3$/AlEt$_2$Cl system[6] are the only reported catalysts capable of serving the dual functions of polymerizing both olefins and polar monomers, such as methyl methacrylate and ϵ-caprolactone, to obtain block copolymers by using the sequential monomer feeding method.

The common synthetic methods used for synthesis of functionalized polyolefin block copolymers are the so-called change of mechanism block copolymerization strategies,[2,3] which combine catalytic olefin polymerization with successive "living"/controlled polymerization of functional monomers (such as anionic polymerization,[7,8] ring-opening polymerization,[9−11] controlled radical polymerization,[4,8,12−15] etc.). These strategies usually involve multiple reaction steps. Generally, telechelic polyolefins end-functionalized with an active group (such as *p*-methyl benzene or vinylbenzene group,[7,8] borane functionality,[12] and hydroxyl group[9−11,13]) are first synthesized by introducing desired chain transfer reactions in olefin polymerization catalyzed mostly by metallocene catalysts. The active chain end groups of the telechelic polyolefins are then transformed into suitable active sites, which act as macroinitiators and further initiate in the third step the successive "living" polymerizations of polar monomers (such as styrene, methyl methacrylates, and ϵ-caprolactone) to give rise to block copolymers.[2,3]

In all the strategies demonstrated so far, synthesis of polyolefins end-capped with an active group and subsequent chain-end transformation to the initiating site for "living" polymerization are critical to obtain the final block copolymers. However, a complete end-group functionalization is always difficult to achieve due to undesirable chain transfer reactions often present in the olefin polymerization step[13] and/or incomplete end-group transformation, which results in incomplete chain extension in the subsequent "living" polymerization step.

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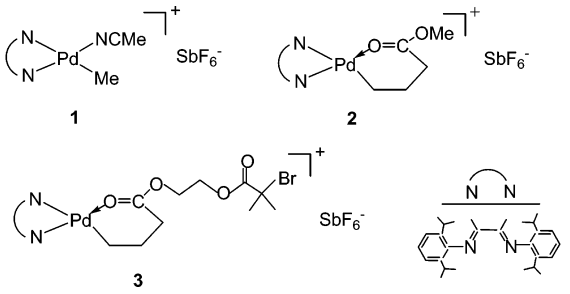
Scheme 1. Structure of Pd−Diimine Complexes



Moreover, the end-functionalized polyolefins generated by chain transfer reactions usually exhibit broad molecular weight distribution (with a PDI of ∼2 in most cases) owing to the nature of metallocene catalysis, leading to final block copolymers with relatively broad distribution. More facile and straightforward methods for the convenient synthesis of polyolefin macroinitiators with narrow polydispersity are, therefore, highly desired for the synthesis of functionalized polyolefin block copolymers with controllable narrow-distributed molecular weights in each constituting block.

Herein, we demonstrate a versatile two-step tandem strategy for synthesis of functionalized polyethylene (PE) block copolymers by combining two "living" polymerization techniques: Pd−diimine catalyzed ethylene "living" polymerization and ATRP. The key to this strategy is the development of a novel functionalized Pd−diimine catalyst, $[(ArN{=}C(Me)-(Me)C{=}NAr)Pd(CH_2)_3C(O)O(CH_2)_2OC(O)C(CH_3)_2Br]^+SbF_6^-$ (Ar = 2,6-(iPr)$_2$C$_6$H$_3$) (**3** in Scheme 1), which enables the direct synthesis of narrow-distributed PEs end-capped with a 2-bromoisobutyryl group via one-step ethylene "living" polymerization. These PEs end-capped with the ATRP initiating site allow direct chain extension via ATRP of styrene and *n*-butyl acrylate to obtain functionalized block copolymers. Compared to other reported synthetic methods for polyolefin block copolymers, this strategy has the remarkable advantages in allowing a precise molecular weight control of each polymer block in the diblock copolymers and being a two-step process without requiring an intermediate functionality transformation step.

Experimental Section

Materials. All manipulations involving air- and/or moisture-sensitive compounds were carried out in a N_2-filled drybox or using Schlenk techniques. The acetonitrile Pd−diimine adduct, $[(ArN{=}C(Me)-(Me)C{=}NAr)Pd(CH_3)(N{\equiv}CMe)]^+SbF_6^-$ (Ar = 2,6-(iPr)$_2$C$_6$H$_3$) (**1**), was synthesized according to the literature procedure.[16] Ultrahigh purity N_2 and polymer-grade ethylene (both obtained from Praxair) were purified by passing through 3Å/5Å molecular sieve and Oxiclear columns to remove moisture and oxygen, respectively, before use. 2-(2-Bromoisobutyryloxy) ethyl acrylate (BIEA) was synthesized by following the literature procedure[18] and was dried over 4 Å molecule sieves. Styrene (99%) and *n*-butyl acrylate (99%) (both from Aldrich) were vacuum distilled before use. Chlorobenzene (99.5%, Aldrich) was refluxed over CaH_2 (powder, 90−95%, Aldrich) and distilled before use. Other chemicals, including anhydrous dichloromethane (99.8%), anhydrous diethyl ether (≥99%), toluene (≥99.5%), methanol (≥99.8%), tetrahydrofuran (THF) (>99%), *N*,*N*,*N*′,*N*″,*N*″-pentamethyldiethylenetriamine (PMDETA) (99%), CuBr (99.999%), $CuBr_2$ (>99%), neutral alumina (∼150 mesh), silica gel (grade 12, 28-200 mesh), etc., were obtained from Aldrich and were used as received.

Synthesis of $[(ArN{=}C(Me)-(Me)C{=}NAr)Pd(CH_2)_3C(O)O(CH_2)_2OC(O)C(CH_3)_2Br]^+SbF_6^-$ (Ar = 2,6−(iPr)$_2$C$_6$H$_3$) (3). A dried Schlenk flask was charged with compound **1** (0.50 g, 6.2×10^{-4} mol), anhydrous diethyl ether (10 mL), and anhydrous dichloromethane (20 mL). BIEA (0.17 g, 6.4×10^{-4} mol, 1.03 equiv) in 5 mL of ether solution was subsequently added. The orange solution was stirred under nitrogen protection for 48 h at room temperature. The resulting solution was filtered, and the solvent was removed in vacuo. The resulting solids were then redissolved in CH_2Cl_2 (5 mL). Pentane (15 mL) was then added slowly to yield an orange precipitate, and the supernatant was decanted carefully. The precipitated solid was washed twice with pentane (15 mL) and dried in vacuo overnight at room temperature, yielding the product as an orange powder of **3** (0.54 g, 85% yield).

^{1}H NMR (500 MHz, CD_2Cl_2, room temp) δ 7.44−7.30 (m, 6H, H_{aryl}), 4.01 (t, 2H, $OC\mathit{H}_2C'H_2O$), 3.50 (t, 2H, $OCH_2C'\mathit{H}_2O$), 2.96 (septet, 2H, $C\mathit{H}Me_2$), 2.94 (septet, 2H, $C''\mathit{H}Me_2$), 2.45 (t, 2H, $PdCH_2CH_2C\mathit{H}_2C(O)$), 2.27 and 2.26 (s, 3 each, $N{=}C(\mathit{Me})-C'(\mathit{Me}){=}N$), 1.89 (s, 6H, $C(O)C\mathit{Me}_2Br$), 1.40 (t, 2H, $PdC\mathit{H}_2$), 1.39, 1.38, 1.34, 1.33, 1.29, 1.28, 1.25, and 1.23 (s, 3 each, $CH\mathit{MeMe'}$, $C'H\mathit{MeMe'}$), 0.68 (pentet, 2H, $PdCH_2C\mathit{H}_2CH_2C(O)$). ^{13}C NMR (125 MHz, CD_2Cl_2, room temp) δ 183.3 ($PdCH_2CH_2CH_2\mathit{C}(O)$), 179.6 and 171.6 ($N{=}\mathit{C}-\mathit{C'}{=}N$), 172.4 ($CH_2O\mathit{C}(O)CMe_2Br$), 141.0 and 140.9 (Ar, Ar′, C_{ipso}), 139.0 and 138.4 (Ar, Ar′, C_o), 129.3 and 128.4 (Ar, Ar′, C_p), 125.0 and 124.7 (Ar, Ar′, C_m), 66.2 and 62.4 ($O\mathit{C}H_2\mathit{C'}H_2O$), 56.1 ($OC(O)\mathit{C}Me_2Br$), 36.1 and 30.4 ($Pd\mathit{C}H_2CH_2\mathit{C}H_2C(O)$), 30.9 ($OC(O)C\mathit{Me}_2Br$), 29.7 and 29.3 ($\mathit{C}HMe_2$, $\mathit{C'}HMe_2$), 23.9 ($PdCH_2\mathit{C}H_2CH_2C(O)$), 24.3, 24.1, 23.5, and 23.4 ($CH\mathit{MeMe'}$, $C'H\mathit{MeMe'}$), 21.9 and 20.2 ($N{=}C(\mathit{Me})-C'(\mathit{Me}){=}N$).

The NMR data indicate the sole presence of a single isomer, the six-membered chelate.

Ethylene "Living" Polymerizations with 3 at 400 psi and 5 °C. Ethylene "living" polymerizations were carried out in a 500 mL Autoclave Engineers Zipperclave reactor equipped with a MagneDrive agitator, a removable heating/cooling jacket, and a sampling port. The reactor temperature was maintained by passing a water/ethylene glycol mixture through the jacket using a refrigerating/heating circulator set at the desired temperature. The reactor was cleaned carefully using acetone, heated overnight at 80 °C under vacuum, then cooled down to 5 °C. Chlorobenzene (250 mL) was then injected into the reactor under N_2 protection. Freshly prepared catalyst **3** solution in chlorobenzene (20 mL, containing 0.2 mmol of catalyst) was subsequently injected into the reactor under N_2 protection. The solution was stirred to establish the equilibrium temperature at 5 °C. The reactor was then quickly pressurized to an ethylene pressure of 400 psi to start the polymerization. During the polymerization, ethylene pressure was maintained at 400 psi and the temperature was controlled at 5 °C by using the circulator. Every hour for 6 h, a 20 mL aliquot of the polymerization solution was taken from the reactor sampling port and the sticky polymer was precipitated out using 2%-acidified methanol. At the end of polymerization run, ethylene pressure was released. The polymer solution was collected and the polymer was obtained by precipitation in a large amount of 2%-acidified methanol. All the polymer samples were redissolved in THF, filtered using a 0.2 μm syringe filter to remove Pd particles, and then precipitated in methanol. Finally the polymer samples were dried in a vacuum oven at 50 °C overnight. The polymer samples were measured using GPC to demonstrate the "living" polymerization nature.

Yield: 1 h, 0.07 g; 2 h, 0.23 g; 3 h, 0.32 g; 4 h, 0.43 g; 5 h, 0.53 g; 6 h, 0.72 g. Gel permeation chromatography (THF, 30 °C, polystyrene reference): 1 h, $M_n = 13.5 \times 10^3$, $M_w/M_n = 1.08$; 2 h, $M_n = 21.3 \times 10^3$, $M_w/M_n = 1.14$; 3 h, $M_n = 32.5 \times 10^3$, $M_w/M_n = 1.11$; 4 h, $M_n = 37.5 \times 10^3$, $M_w/M_n = 1.15$; 5 h, $M_n = 43.0 \times 10^3$, $M_w/M_n = 1.17$; 6 h, $M_n = 46.0 \times 10^3$, $M_w/M_n = 1.21$. ^{1}H NMR ($CDCl_3$, 200 MHz, room temp, δ): 4.35 (m, 4H, $OC\mathit{H}_2C'\mathit{H}_2O$), 2.33 (t, 2H, $C(O)C\mathit{H}_2$-polymer), 1.94 (s, 6H, $C(O)C\mathit{Me}_2Br$), 1.26 (polymer $C\mathit{H}_2$), 1.22 (polymer $C\mathit{H}$), 0.85 (m, polymer $C\mathit{H}_3$). Branching density (by ^{1}H NMR): 1 h, 89 branches/1000 C; 2 h, 87 branches/1000 C; 3 h, 88 branches/1000 C; 4 h, 87 branches/1000 C; 5 h, 82 branches/1000 C; 6 h, 86 branches/1000 C.

Two separate ethylene "living" polymerization runs were conducted for 1 and 3 h only to prepare the PE macroinitiators for ATRP, PEMI-1, and PEMI-2, respectively. The above polymerization procedure was followed, except using different solvent amount (200 mL of chlorobenzene) and catalyst amount (0.4 and 0.2 mmol of **3** for PEMI-1 and PEMI-2, respectively). During the polymerization, no polymer solution was sampled. After the polymerization, the polymer was precipitated out in a large amount of acidified methanol. The polymer samples were redissolved in THF and passed through a silica/alumina column to remove Pd particles until becoming colorless solutions. The polymers were finally precipitated out and washed using methanol and then dried in a vacuum oven for 2 days at 50 °C. Yield: PEMI-1, ~1.9 g; PEMI-2, ~3.2 g. Gel permeation chromatography (THF, 30 °C, polystyrene reference): PEMI-1, $M_n = 12.8 \times 10^3$, $M_w/M_n = 1.12$; PEMI-2, $M_n = 30.6 \times 10^3$, $M_w/M_n = 1.13$. Branching density (by ^{1}H NMR): PEMI-1, 80 branches/1000 C; PEMI-2, 85 branches/1000 C. Turnover frequency (by end groups in ^{1}H NMR): PEMI-1, 335/h; PEMI-2, 290/h.

Synthesis of Block Copolymers by ATRP of Styrene and *n*-Butyl Acrylate with Polyethylene Macroinitiators. The following is a typical ATRP procedure (Run 3 in Table 4). The PE macroinitiator (PEMI-2, 0.351 g, 0.014 mmol), toluene (2.5 mL), styrene (2.5 mL, 22 mmol), CuBr (12.0 mg, 0.084 mmol), $CuBr_2$ (1.9 mg, 0.0084 mmol), and PMDETA (16.0 mg, 0.0924 mmol) were added to a 20 mL glass reactor. The reactor was sealed with a rubber septum and degassed with dry N_2 for 10 min. The reaction mixture was then subject to three freeze−pump−thaw cycles and finally filled with nitrogen. After stirring the reaction mixture for 10 min at room temperature, the reactor was placed in a thermostated oil bath at 100 °C and protected with dry N_2 throughout the polymerization. Samples were removed at different time intervals during polymerization to monitor monomer conversion (calculated based on the molar ratio between styrene and ethylene units from ^{1}H NMR spectroscopy) and molecular weight of the block copolymers using gel permeation chromatography. The block copolymers were obtained by precipitation using acidified methanol and were washed with a large amount of methanol three times. The polymers were dried under vacuum at 50 °C overnight.

Conversion (calculated from polymer ^{1}H NMR spectroscopy): 0.5 h, 1.0%; 1 h, 2.1%; 2 h, 3.5%; 3 h, 6.3%; 6 h, 7.0%; 10 h, 9.3%. Gel permeation chromatography (THF, 30 °C, polystyrene reference): 0.5 h, $M_n = 32.1 \times 10^3$, $M_w/M_n = 1.15$; 1 h, $M_n = 34.0 \times 10^3$, $M_w/M_n = 1.14$; 2 h, $M_n = 34.8 \times 10^3$, $M_w/M_n = 1.18$; 3 h, $M_n = 39.9 \times 10^3$, $M_w/M_n = 1.25$; 6 h, $M_n = 41.9 \times 10^3$, $M_w/M_n = 1.31$; 10 h, $M_n = 43.9 \times 10^3$, $M_w/M_n = 1.36$.

Characterizations and Measurements. ^{1}H (500 MHz) and ^{13}C (125 MHz) nuclear magnetic resonance (NMR) spectra of the organometallic Pd−diimine compounds were obtained on a Bruker AV500 spectrometer at ambient temperature with CD_2Cl_2 as the solvent. ^{1}H NMR spectra (200 MHz) of the polymer samples were all obtained on a Varian Gemini 2000 spectrometer at ambient temperature. $CDCl_3$ was used as the solvent for polyethylene macroinitiators and polyethylene-*b*-poly(*n*-butyl acrylate) block copolymers, and CD_2Cl_2 was used as the solvent for polyethylene-*b*-polystyrene block copolymers. ^{13}C NMR spectra (125 MHz) of the two polyethylene macroinitiators (PEMI-1 and PEMI-2) were obtained on a Bruker AV500 spectrometer at ambient temperature with $CDCl_3$ as the solvent.

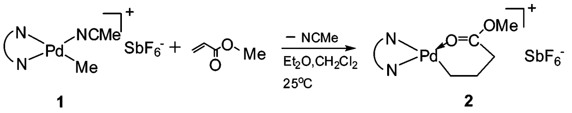
Single-crystal X-ray diffraction (XRD) measurement was conducted on a Bruker SMART APEX2 Mo diffractometer at −100 °C. A single crystal of **3** was placed on the end of a MiTeGen crystal mount with paratone oil and centered on the diffractometer. The unit cell was determined and a complete diffraction data set was collected to $2\theta = 65°$ using φ and ω scans. A numerical face correction was applied to the integrated data. The structure was solved using direct methods and refined by least-squares. The structure (cation, anion, and lattice solvent) showed disorder in various groups and restraints were required for successful refinement. Hydrogen atoms were placed in calculated positions.

Gel permeation chromatography (GPC) measurements were performed on a Polymer Laboratory PL-GPC220 system equipped with a differential refractive index detector, one guard column (PL 1110−1120), and three Polymer Laboratory 30 cm mixed columns (PLgel 10 μm MIXED-B 300 × 7.5 mm, linear range of molecular weight: 500−10 000 000 g/mol). The system operated at 30 °C, and THF was used as the eluent at a flow rate of 1.0 mL/min. Polystyrene standards (PL EasiVials) covering molecular weights from 580 to 6 035 000 g/mol were used for the column calibration.

Differential scanning calorimetry (DSC) analysis was performed on a TA Instruments Q100 DSC equipped with a refrigerated cooling system (RCS) under a N_2 atmosphere. The instrument was operated in the standard DSC mode and was calibrated with an indium standard. A N_2 purging flow of 50 mL/min was used. Samples (~5 mg) were heated from room temperature to 150 °C at 10 °C/min and cooled to −90 °C at 5 °C/min, and the data were then collected on the second heating ramp from −90 °C to 150 °C at 10 °C/min. Glass transition temperatures (T_g) were read as the middle of the change in heat capacity. The melting temperatures (T_m) were read as the maximum of the endothermic peaks.

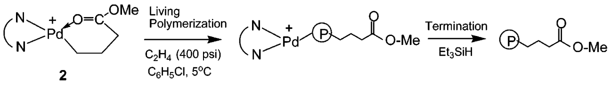
Results and Discussion

Synthesis and Characterization of Functionalized Pd−Diimine Catalyst, [(ArN═C(Me)−(Me)C═NAr)Pd(CH$_2$)$_3$C(O)O(CH$_2$)$_2$OC(O)C(CH$_3$)$_2$Br]$^+$SbF$_6^-$ (Ar = 2,6-(*i*Pr)$_2$C$_6$H$_3$) (3). Pd−diimine catalysts are a novel series of late transition metal catalysts for catalytic olefin polymerization.[16,17] The catalysts have high versatility in catalyzing "living" polymerization of ethylene and α-olefin under certain conditions,[19] besides possessing the unique chain walking mechanism[20,21] and outstanding tolerance toward polar functional groups.[22] The acetonitrile adduct **1** and chelate complex **2** shown in Scheme 1 are typical Pd−diimine catalysts used for "living" polymerization of ethylene and olefins.[19] Specifically, the chelate complex **2** can be synthesized by reaction of **1** with methyl acrylate (eq 1), in which the acrylate is inserted into the Pd−Me bond of **1** via a 2,1-insertion mechanism followed by rearrangement (via β-hydride elimination and reinsertion) to form the six-membered chelate.[22]



(1)

Complex **2** is uniquely capable of generating telechelic polymers end-functionalized with an ester group in ethylene "living" polymerization. During the "living" polymerization, chain propagation starts by monomer insertion into the Pd−CH$_2$ bond and this yields polymer chains end-capped with a methyl ester group (eq 2), which is introduced at the beginning of the chain growth.[19]



(2)

The unique synthesis and polymerization chemistry of the chelate complex has allowed the versatile synthesis of telechelic polyethylenes by "living" polymerization using functionalized Pd−diimine chelate complexes synthesized by reacting **1** with functional acrylate monomers. For example, Matyjaszewski et al.[23] reported the synthesis of polyethylene macromonomers end-capped with a methacrylate functionality by ethylene "living" polymerization using a functionalized Pd−diimine chelate

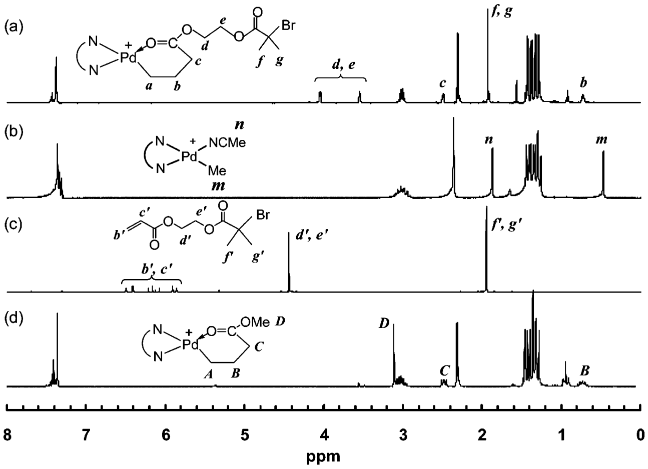
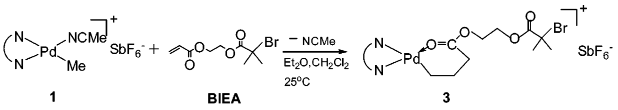


Figure 1. ^{1}H nuclear magnetic resonance spectrum of (a) **3**, (b) **1**, (c) 2-(2-bromoisobutyryloxy) ethyl acrylate, and (d) **2**.[24] Peaks for a and A overlap with the peaks for methyl protons (1.2−1.45 ppm) on the isopropyl groups of the diimine ligand.

complex, which was synthesized by reacting **1** with a functionalized acrylate, acryloyloxyethyl methacrylate bearing both acrylate and methacrylate functionalities. We have also synthesized binuclear Pd−diimine catalysts by reacting **1** with diacrylate monomers for bifunctional ethylene "living" polymerization.[24]

Utilizing this chemistry, we synthesized in this work a novel functionalized Pd−diimine catalyst, **3**, by reacting **1** with a functional acrylate monomer bearing a 2-bromoisobutyryl group, 2-(2-bromoisobutyryloxy) ethyl acrylate (BIEA). BIEA is a typical ATRP inimer for the synthesis of hyperbranched polymers by self-condensing vinyl polymerization.[18] The Pd−diimine catalysts are stable toward the 2-bromoisobutyryl functionality.[25] Recently, we have demonstrated the copolymerization of ethylene with BIEA using **1** as the catalyst to directly synthesize hyperbranched polyethylenes tethered with 2-bromoisobutyryl functionalities as polyfunctional macroinitiators for ATRP.[26] Insertion of the acrylate group of BIEA into the Pd−Me bond of **1** via a 2,1-insertion mechanism followed by rearrangement leads to the functionalized chelate compound, **3**, bearing an intact pendant 2-bromoisobutyryl substituting group on the six-membered chelate structure (eq 3).[22]



(3)

Ethylene "living" polymerization with **3** as the catalyst is expected to give rise to telechelic PEs end-functionalized with a terminal 2-bromoisobutyryl functionality, which can further be used as macroinitiators in a subsequent ATRP step to obtain block copolymers.

The structure of the functionalized Pd−diimine complex, **3**, is confirmed by using NMR spectroscopy. Figure 1 shows the ^{1}H NMR spectrum of **3** along with those of **1**, **2**, and BIEA for comparison. The resonance peaks at 0.46 ppm for Pd*Me* and 1.81 ppm for PdNC*Me* in **1** (m and n in Figure 1b, respectively) are absent in the spectrum of **3** (Figure 1a), showing the absence of unreacted **1** in **3**. There are no peaks observed in the vinyl double bond region, showing the absence of unreacted BIEA. The six-membered chelate structure in **3** is validated from the peaks at 2.42 ppm for $PdCH_2CH_2C\mathit{H}_2C(O)$ (c in Figure 1a) and 0.67 ppm for $PdCH_2C\mathit{H}_2CH_2C(O)$ (b in Figure 1a), which are identical to those found in **2** (C and B, respectively, in Figure 1d).[22−24] The presence of the pendant 2-bromoisobutyryl functionality in **3** is validated based on the methylene resonances at 4.03 and 3.53 ppm (d, e), and the methyl resonance at 1.92 ppm (f, g). The integration ratio between the methylene and methyl resonances is 2:3, indicating the intactness of the 2-bromoisobutyryl functionality. Within the precision limit, integration of the resonance peaks agrees well to the catalyst structure. ^{13}C NMR analysis also confirms the structure of **3**.[27] As shown by Brookhart et al.,[22] the five-membered chelate isomer is often found in Pd−diimine chelate complexes though the six-membered chelate is always predominant. In the ^{13}C NMR spectra, a resonance peak at 194.3 ppm for *C*(O) on the chelate is typically found with the five-membered chelate isomer resulting from 1,2-insertion of the acrylate group into the Pd−Me of **1** followed by rearrangement.[22] Differently, for the six-membered chelate, the peak for *C*(O) on the chelate is located at 183.0 ppm.[22] In the ^{13}C NMR spectra of **3**, only the resonance at 183.0 ppm is observed, suggesting the absence of the five-membered chelate isomer.

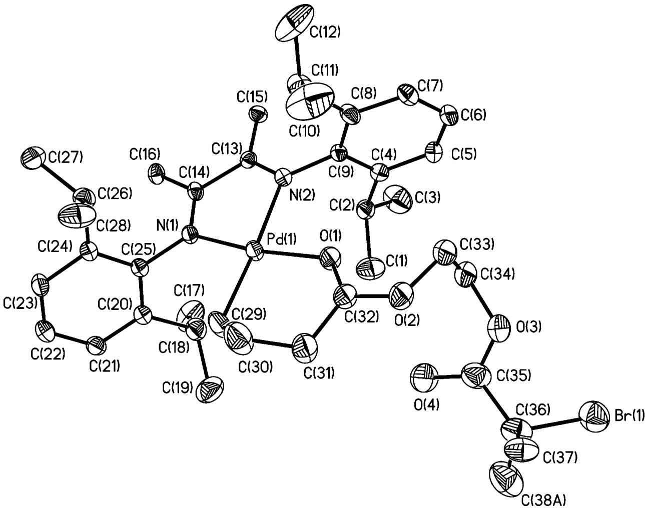


Figure 2. Thermal ellipsoid (30% probability) of **3**. Hydrogen atoms, anion, solvent molecules, and the disordered parts of the structure are omitted. Selected bond lengths (Å) and angles (deg): Pd(1)−N(1) = 2.022(7), Pd(1)−N(2) = 2.138(7), Pd(1)−C(29) = 2.020(9), Pd(1)−O(1) = 2.057(6); N(1)−Pd(1)−N(2) = 78.0(3), N(1)−Pd(1)−C(29) = 96.6(3), C(29)−Pd(1)−O(1) = 91.2(3), O(1)−Pd(1)−N(2) = 94.2(2), N(1)−Pd(1)−O(1) = 172.2(2), C(29)−Pd(1)−N(2) = 174.5(3).[28]

The structure of **3** is also confirmed by using single-crystal X-ray diffraction (XRD) measurement. Single crystals of **3** were obtained by slow diffusion of pentane and diethyl ether into a dichloromethane solution at room temperature for 4 days under a nitrogen atmosphere. X-ray diffraction measurement was carried out on a suitable single crystal, and the molecular structure of **3** was thus elucidated. Figure 2 shows the thermal ellipsoid plot of the complex, which clearly evidences the six-membered chelate structure containing the tethered 2-bromoisobutyryl group.[28] Pentane molecules are incorporated in the crystal lattice, and the SbF_6^- anion is far apart and does not show interaction with the metal center. Like the other reported Pd−diimine complexes, the sterically bulky isopropyl substituted aryl rings are nearly perpendicular to the plane of the butandiimino moiety with the dihedral angles of 82.96° and 83.34°, respectively. The bond length of Pd(1)−N(1) is shorter than that of Pd(1)−N(2) (2.022(7) vs 2.138(7) Å), which indirectly reflects that the interaction of Pd(1) and O(1) is weaker than that of Pd(1) and C(29).[29] The Pd(1)−O(1) bond distance (2.057(6) Å) is comparable to the corresponding distances in the palladium carboxylates (1.99−2.12 Å).[30]

Scheme 2. Tandem Strategy for Synthesis of Functionalized Polyethylene Block Copolymers, Where PE = Polyethylene; BA = *n*-Butyl Acrylate; S = Styrene; ATRP = Atom Transfer Radical Polymerization; PBA = Poly(*n*-butyl acrylate); PS = Polystyrene

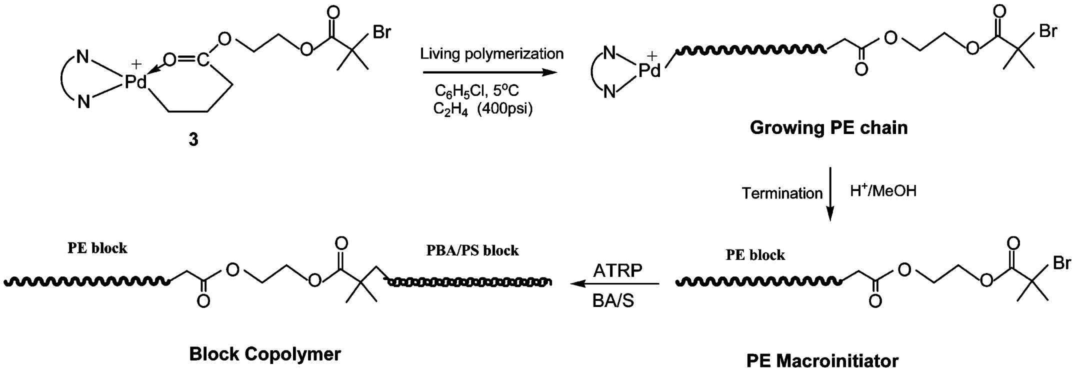


Table 1. "Living" Polymerization of Ethylene with 3 at 5 °C and 400 psi in Chlorobenzene[a]

entry	time (h)	$M_{n,GPC}$[b] (kg/mol)	PDI[b]	$M_{n,NMR}$[c] (kg/mol)	TOF_{NMR}[d] (1/h)	$M_{n,Grav}$[e] (kg/mol)	TOF_{Grav}[e] (1/h)	branches[f] (per 1000 C)
1	1	13.5	1.08	8.9	316	4.3	154	89
2	2	21.3	1.14	16.4	292	14.1	251	87
3	3	32.5	1.11	24.8	295	19.7	235	88
4	4	37.5	1.15	31.9	285	27.0	241	87
5	5	43.0	1.17	40.4	288	33.6	240	82
6	6	46.0	1.21	46.3	275	44.7	266	86

[a] Other conditions: catalyst **3** amount, 0.2 mmol; total volume, 200 mL. [b] Number-average molecular weight ($M_{n,GPC}$) and polydispersity index (PDI) determined by gel permeation chromatography vs polystyrene standards. [c] Number-average molecular weight ($M_{n,NMR}$) determined by ^{1}H nuclear magnetic resonance spectroscopy based on end group analysis. [d] Turnover frequency (TOF_{NMR}) determined from ^{1}H nuclear magnetic resonance spectroscopy based on end group analysis. [e] Number-average molecular weight ($M_{n,Grav}$) and turnover frequency (TOF_{Grav}) determined gravimetrically on the basis of moles of catalyst employed and the weight of polymer produced per hour for each aliquot. [f] Total branching determined from ^{1}H nuclear magnetic resonance spectroscopy.

Ethylene "Living" Polymerization Using 3 at 400 psi and 5 °C. Scheme 2 illustrates the two-step tandem strategy employed here for synthesis of block copolymers. The first step involves ethylene "living" polymerization with **3** as the catalyst. Because of the unique chelate structure of **3**, ethylene "living" polymerization directly leads to telechelic PE chains end-capped with a terminal 2-bromoisobutyryl functionality, which is introduced at the beginning of chain growth. This is distinctly different from the conventional approaches for telechelic PEs, where the terminal functional group is often introduced at the end of the growing chain via a chain transfer/termination reaction. This unique feature also guarantees the complete end-functionalization of each PE chain produced via "living" polymerization with **3**.

Ethylene "living" polymerization with **3** was carried out at an ethylene pressure of 400 psi and a temperature of 5 °C, a typical condition for ethylene "living" polymerization with Pd−diimine catalysts.[19] To demonstrate the "living" nature of the polymerization, aliquots of the polymerization solution in chlorobenzene were removed every hour for 6 h during polymerization for monitoring molecular weight development. The aliquot polymer solutions were quenched by direct precipitation in a large amount of 2%-acidified methanol. In the literature, the growing polymer chains by Pd−diimine catalysts are usually quenched by using Et_3SiH.[19] It was reported that quenching of the polymer with acidified methanol yielded chain coupling.[19] However, based on NMR analyses of the quenched polymers, we found in our study that Et_3SiH reacted with the bromide-containing 2-bromoisobutyryl terminal groups even at a low concentration with a 1:1 molar ratio between [Et_3SiH] and [**3**], leading to the partial loss of 2-bromoisobutyryl chain end functionality. On the contrary, no chain coupling was detected for polymers quenched using acidified methanol based on their GPC elution traces and their 2-bromoisobutyryl functionality remained intact from ^{1}H NMR end group analysis.

Table 1 summarizes the results of "living" polymerization of ethylene with **3** in chlorobenzene. Figure 3a shows the monomodal GPC elution curves of the PE samples as a function of polymerization time. Figure 3b plots the number-average molecular weight ($M_{n,GPC}$) and polydispersity index (PDI), determined from GPC measurements using a relative calibration curve generated based on polystyrene standards, vs polymerization time. A close-to-linear increase of polymer molecular weight with time is evident. The PDI values of these samples are low (within 1.08−1.21), characteristic of "living" polymerization. ^{1}H NMR measurements were performed to elucidate polymer microstructure and confirm the presence of the 2-bromoisobutyryl end-functionality. Figure 4 shows the ^{1}H NMR spectra of the PE samples taken at 1 and 3 h, respectively, of "living" polymerization. The resonance peaks (h, d″, e″, f″, and g″) from the 2-bromoisobutyryl functionality are clearly present in both spectra. Integration shows that the molar ratio of methyl protons (f″, g″)/methylene protons (d″, e″) is 3:2, indicating the 2-bromoisobutyryl functionalities are intact without loss during quenching of the polymer with acidified methanol.

Calculations based on the resonances of methylene, methine, and methyl protons of the ethylene sequence on the polymer backbone indicate that the polymers are all highly branched with approximately 87 branches per 1000 carbons (Table 1). Such a highly branched chain structure is a result of the chain walking mechanism of the Pd−diimine catalyst.[20,21] On the basis of our prior studies,[21] the chain topology of these polymers, however, should still be linear with a linear backbone grafted with mainly short branches given the polymerization condition of 400 psi and 5 °C. On the basis of the fact that each polymer chain contains one end-capping 2-bromoisobutyryl functionality, the number-average molecular weights, $M_{n,NMR}$, of the polymer samples were also calculated based on their ^{1}H NMR spectra (see Table 1). These data are also plotted in Figure 3b as a

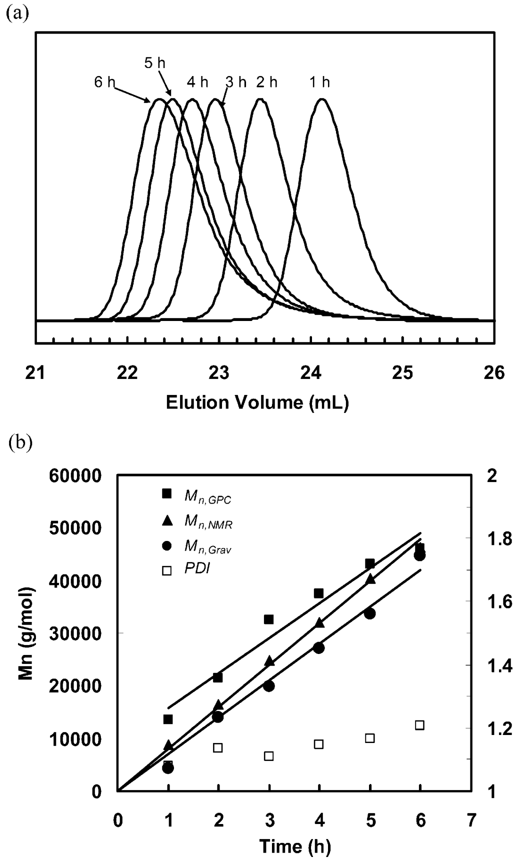


Figure 3. (a) Gel permeation chromatography elution traces of telechelic polyethylene samples obtained at different polymerization time in ethylene "living" polymerization with **3** at 400 psi and 5 °C and (b) plot of polymer number-average molecular weight (M_n) and polydispersity index (PDI) as functions of polymerization time.

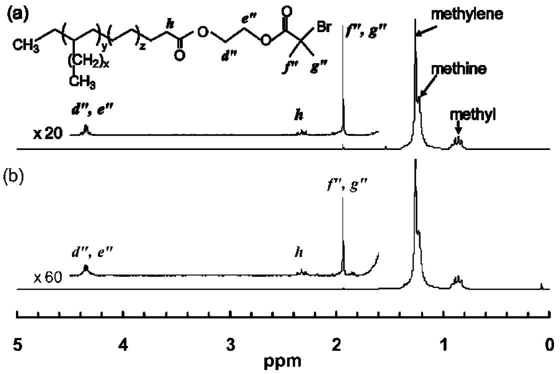


Figure 4. ^{1}H nuclear magnetic resonance spectrum of telechelic polyethylene sample obtained at (a) 1 h and (b) 3 h in ethylene "living" polymerization with **3** at 400 psi and 5 °C.

function of polymerization time. A much better linearity is observed with $M_{n,NMR}$ vs polymerization time, compared to $M_{n,GPC}$ vs time. Because of the differences in the hydrodynamic volumes of these branched PEs and polystyrene standards, $M_{n,GPC}$ determined for these polymers is relative data and does not match $M_{n,NMR}$, which reflects the true number-average molecular weight of the polymers. Similarly, the turnover frequency (TOF_{NMR}) values were also calculated using the $M_{n,NMR}$ results. As shown in Table 1, the TOF_{NMR} value decreases slightly from 316/h to 275/h with the increase of polymerization time from 1 to 6 h, indicating the deactivation of some growing chains, though at a low level, during the polymerization. However, this TOF range is quite close to the TOF values we obtained from ^{1}H NMR spectroscopy for ethylene "living" polymerization catalyzed by **2** at the same condition.[24]

Table 2. Polyethylene Macroinitiators Synthesized for Atom-Transfer Radical Polymerization

macroinitiator	polymerization time[a] (h)	$M_{n,GPC}$[b] (kg/mol)	PDI [b]	$M_{n,NMR}$[c] (kg/mol)
PEMI-1	1	12.8	1.12	9.4
PEMI-2	3	30.6	1.13	24.4

[a] Other conditions: catalyst **3** amount, 0.4 mmol for PEMI-1 and 0.2 mmol for PEMI-2; solvent, chlorobenzene; total volume, 200 mL. [b] Number-average molecular weight ($M_{n,GPC}$) and polydispersity index (PDI) determined by gel permeation chromatography vs polystyrene standards. [c] Number-average molecular weight ($M_{n,NMR}$) determined by ^{1}H nuclear magnetic resonance spectroscopy based on end group analysis.

With the use of the weights of the polymers obtained in each aliquot, the number-average molecular weights ($M_{n,Grav}$) and turnover frequency data (TOF_{Grav}) were calculated gravimetrically on the basis of moles of catalyst employed and the weight of polymer produced per hour.[19] These data are listed in Table 1 as well. They were obtained based on the assumption that there was no catalyst deactivation and each Pd metal center initiated successfully the growth of one polymer chain. They thus represent theoretical molecular weight and turnover frequency data. As shown in Table 1, the average TOF_{Grav} value is about 240/h, very close to those reported in the literature, which were also calculated using the same gravimetric method, for ethylene "living" polymerization with catalyst **1** and **2** under similar polymerization conditions.[19] This resemblance is a result of the fact that the three cationic Pd catalysts possess the same chain growing metal centers though having different functionalities introduced at the beginning of chain growth. However, compared to TOF_{NMR} data determined from ^{1}H NMR spectroscopy, the TOF_{Grav} data are generally lower. As shown in Figure 3b, linear increase of $M_{n,Grav}$ with time is also observed. Correspondingly, the $M_{n,Grav}$ data are always slightly lower than $M_{n,NMR}$. The lower TOF_{Grav} and $M_{n,Grav}$ values thus demonstrate the presence of incomplete catalyst initiation and/or catalyst deactivation in the polymerization.

Because of the presence of end-tethered 2-bromoisobutyryl functionality, which is active for initiating ATRP, the telechelic PEs synthesized by ethylene "living" polymerization with **3** can be directly used as macroinitiators for ATRP to obtain block copolymers. The chain length of these PE-based macroinitiators can be conveniently controlled by adjusting the time of ethylene "living" polymerization to obtain a desired length of PE block in the ultimate block copolymers. In the second step of this tandem strategy for block copolymers (Scheme 2), ATRPs of styrene and *n*-butyl acrylate were carried out using two PE macroinitiators, PEMI-1 and PEMI-2, of different chain lengths. These two PE macroinitiators were synthesized separately in two additional ethylene "living" polymerization runs under 400 psi and 5 °C with the polymerization time of 1 and 3 h, respectively, to produce sufficient polymer amounts for subsequent ATRP runs. Table 2 summarizes the molecular weight data of these two macroinitiators. Both macroinitiators have a low PDI of about 1.12. Slight differences in molecular weight, but within error range, are observed compared to the data shown in Table 1 for corresponding polymers obtained at the same polymerization time. This should be due to some very minor differences in the polymerizations and/or polymer characterizations.

The branching structure of these two polyethylene macroinitiators was elucidated using ^{13}C NMR spectroscopy. Representatively, Figure 5 shows the ^{13}C NMR spectrum of PEMI-1.

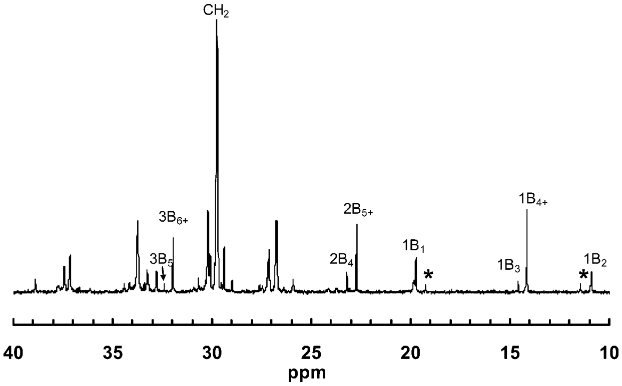


Figure 5. ^{13}C nuclear magnetic resonance spectrum of the polyethylene macroinitiator, PEMI-1, synthesized in ethylene "living" polymerization with **3** at 400 psi and 5 °C with polymerization time of 1 h. The two peaks marked by the asterisk (∗) represent methyls of the methyl and ethyl branches, respectively, of the *sec*-butyl ended branch.[17,20]

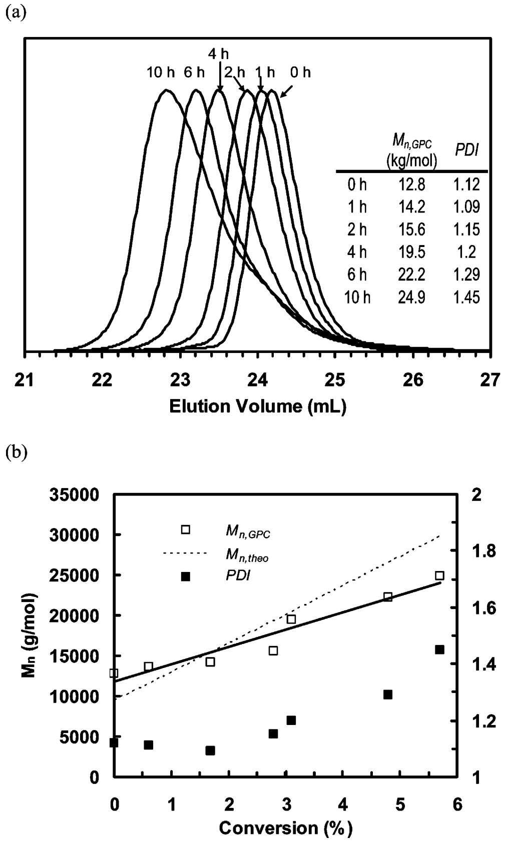
Table 3. Short Chain Branching Distribution Determined from ^{13}C Nuclear Magnetic Resonance Spectroscopy for the Two Polyethylene Macroinitiators in Number of Branches Per 1000 Carbons[a]

polymer	methyl	ethyl	propyl	butyl	amyl	hexyl+	% B[b]	total branch
PEMI-1	34.7	12.9	3.8	6.1	3.5	29.1	9.3	90
PEMI-2	37.0	12.2	5.0	5.7	3.8	28.2	10.3	92

[a] ^{13}C nuclear magnetic resonance (125 MHz) spectra were obtained with CDCl$_3$ as the solvent at ambient temperature. [b] Percentage of methyl from *sec*-butyl branches in the total methyl branches.

The unique carbon resonances of different short branches from methyl to hexyl and longer can be identified, which allow the calculation of the density of each branching type per 1000 carbons in the polymers.[17,20] In addition, the smallest branch-on-branch structure, *sec*-butyl group (evidenced by the two peaks marked by asterisks in Figure 5), is also observed in the ^{13}C NMR spectra of both polymers, which indicates the occurrence of chain walking through a tertiary carbon.[17,20] Table 3 lists the branching distribution in the two polymers.

Synthesis of Block Copolymers by ATRP of Styrene and *n*-Butyl Acrylate with Polyethylene Macroinitiators. We demonstrate four representative ATRP runs conducted using PEMI-1 and PEMI-2 as macroinitiators. Table 4 summarizes the conditions for the synthesis of polyethylene-*b*-polystyrene (PE-*b*-PS) and polyethylene-*b*-poly(*n*-butyl acrylate) (PE-*b*-PBA) block copolymers. In ATRP using macroinitiators, a common challenge is to minimize both radical coupling and incomplete chain initiation in order to obtain block copolymers of low polydispersity. We optimized to use low macroinitiator concentrations (1.3×10^{-3} M for runs 1 and 2, 2.9×10^{-3} M for runs 3 and 4) in this work, together with the initial addition of a small amount of Cu^{2+} (10 mol % of Cu^{+}) as deactivator to suppress the radical concentration and subsequently reduce radical coupling in the polymerization system.[31] High ratios of $[\mathrm{Cu}^{+}]_0/[\mathrm{I}]_0$ were used in our polymerization systems for the purpose of enhancing initiation efficiency. CuBr/CuBr$_2$/PMDETA was used as the catalyst system for all ATRP runs along with the choice of toluene as the solvent. Monomer conversions were also restricted to minimize chain transfer/coupling reactions. Because of the highly branched structure, the PE macroinitiators are completely amorphous at room temperature and have good solubility in toluene even at room temperature.



	$M_{n,GPC}$ (kg/mol)	PDI
0 h	12.8	1.12
1 h	14.2	1.09
2 h	15.6	1.15
4 h	19.5	1.2
6 h	22.2	1.29
10 h	24.9	1.45

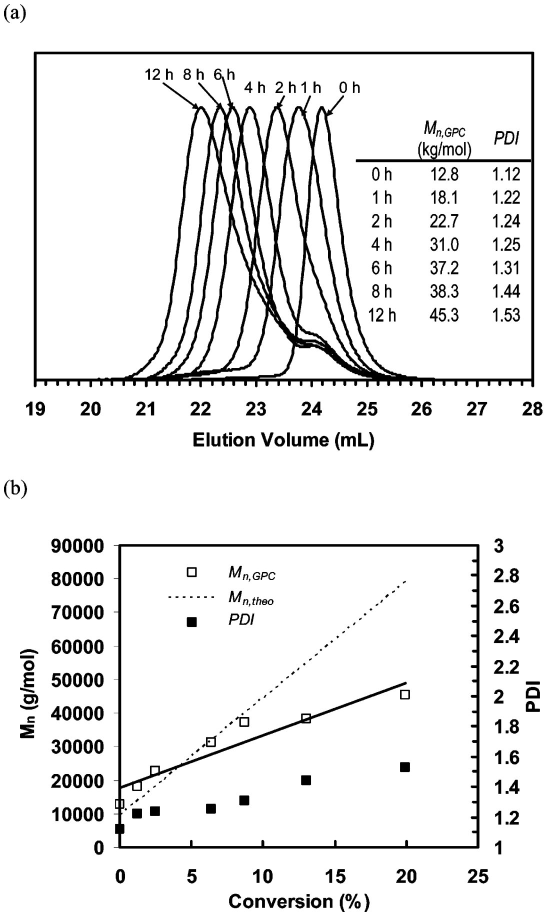
Figure 6. (a) Gel permeation chromatography elution traces and (b) number-average molecular weight (M_n) and polydispersity index (PDI) vs conversion for polyethylene-*b*-polystyrene block copolymers synthesized in atom-transfer radical polymerization of styrene with PEMI-1 (run 1).

Figure 6 shows the results of styrene polymerization using PEMI-1 as the initiator at 100 °C (run 1). With an increase of polymerization time, the molecular weight of the polymers shows consistent increase from the GPC traces (Figure 6a) of polymer samples taken at different polymerization time, demonstrating the successful chain extension and the yielding of polyethylene-*b*-polystyrene (PE-*b*-PS) diblock copolymers. Figure 6b shows that the number-average molecular weights ($M_{n,GPC}$), measured by GPC based on polystyrene standards, increases almost linearly with monomer conversion, indicating the "livingness" and good control of the polymerization. All block copolymer samples obtained at different polymerization time show monomodal molecular weight distribution. High-molecular-weight shoulders are not seen in the GPC elution traces, suggesting the absence of radical coupling at the low

Table 4. Atom-Transfer Radical Polymerization Conditions for Synthesis of Polyethylene-*b*-polystyrene and Polyethylene-*b*-poly(*n*-butyl acrylate) Block Copolymers Using Polyethylene Macroinitiators[a]

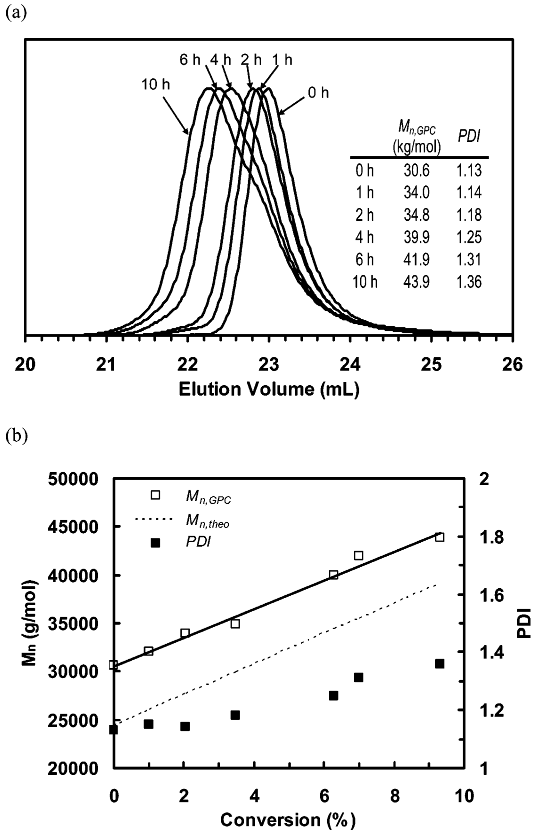
run	$[\mathrm{M}]_0/[\mathrm{I}]_0/[\mathrm{CuBr}]_0/[\mathrm{CuBr_2}]_0/[\mathrm{L}]_0$	macroinitiator and concentration (M)	monomer and concentration (M)	temperature (°C)
1	3400:1:12:1.2:13.2	PEMI-1, 1.3×10^{-3}	styrene, 4.4	100
2	2700:1:12:1.2:13.2	PEMI-1, 1.3×10^{-3}	*n*-butyl acrylate, 3.5	90
3	1500:1:6:0.6:6.6	PEMI-2, 2.9×10^{-3}	styrene, 4.4	100
4	1200:1:6:0.6:6.6	PEMI-2, 2.9×10^{-3}	*n*-butyl acrylate, 3.5	90

[a] Other conditions: solvent, toluene; L = *N,N,N′,N″,N″*-pentamethyldiethylenetriamine; M = monomer; I = macroinitiator.



	$M_{n,GPC}$ (kg/mol)	*PDI*
0 h	12.8	1.12
1 h	18.1	1.22
2 h	22.7	1.24
4 h	31.0	1.25
6 h	37.2	1.31
8 h	38.3	1.44
12 h	45.3	1.53

Figure 7. (a) Gel permeation chromatography elution traces and (b) number-average molecular weight (M_n) and polydispersity index (PDI) vs conversion for polyethylene-*b*-poly(*n*-butyl acrylate) block copolymers synthesized in the atom-transfer radical polymerization of *n*-butyl acrylate with PEMI-1 (run 2).



	$M_{n,GPC}$ (kg/mol)	*PDI*
0 h	30.6	1.13
1 h	34.0	1.14
2 h	34.8	1.18
4 h	39.9	1.25
6 h	41.9	1.31
10 h	43.9	1.36

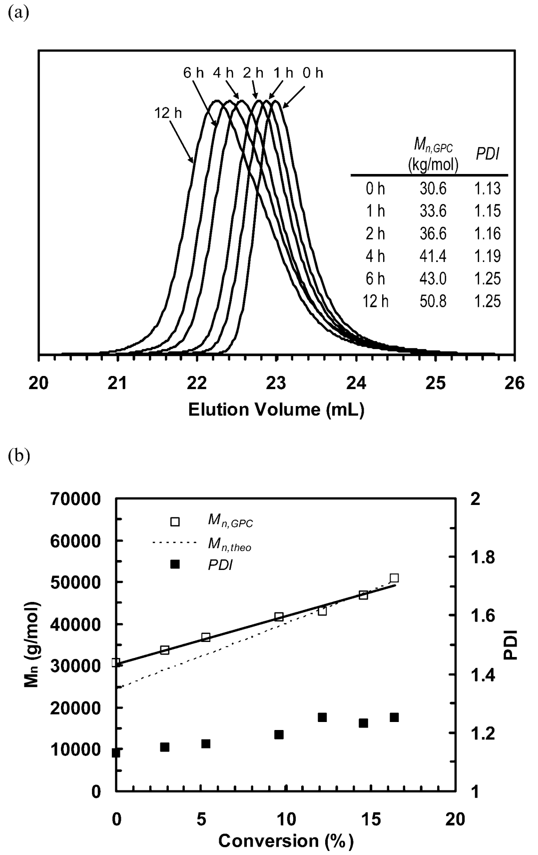
Figure 8. (a) Gel permeation chromatography elution traces and (b) number-average molecular weight (M_n) and polydispersity index (PDI) vs conversion for polyethylene-*b*-polystyrene block copolymers synthesized in the atom-transfer radical polymerization of styrene with PEMI-2 (run 3).

macroinitiator concentration of 1.3 × 10 $^{-3}$ M. Weak low-molecular-weight tails are seen in the GPC traces after 6 h of polymerization. With the increase of polymerization time, the molecular weight distribution broadens slightly from the increase of the PDI value. However, the block copolymers generally possess a narrow molecular weight distribution with a PDI of 1.29 at 6 h of polymerization.

ATRP of *n*-butyl acrylate was also carried out from PEMI-1 at 90 °C (run 2) to synthesize polyethylene-*b*-poly(*n*-butyl acrylate) (PE-*b*-PBA) diblock copolymers. Successful chain extension was also achieved. Figure 7 demonstrates the polymerization behavior of run 2, and it can be seen that there is a consistent increase of copolymer molecular weight with polymerization time. The number-average molecular weight exhibits a close-to-linear dependency on monomer conversion as shown in Figure 7b. Radical coupling is not observed from the absence of high-molecular-weight shoulders in Figure 7a. However, a weak low-molecular-weight shoulder peak appears obviously after 2 h of polymerization. The elution volume of this shoulder peak is very close to that of PEMI-1 and does not decrease with the increase of polymerization time, indicating that this shoulder peak should be attributed to a small portion of dead polymer chains resulting from deactivation reactions. The intensity of the shoulder peak remains quite constant regardless of polymerization time, suggesting that the portion of these dead chains does not increase during polymerization. Accordingly, the PDI of the block copolymer increases slightly due to these dead polymers. At 6 h, the block copolymer obtained has a $M_{\mathrm{n,GPC}}$ value of 37.2 kg/mol with a PDI of 1.31. Further polymerization leads to a further slight broadening in polymer molecular weight distribution.

Block copolymers were also successfully synthesized in runs 3 and 4 by chain extension from PEMI-2, which has higher molecular weight than PEMI-1. Figures 8 and 9 summarize the polymerization of styrene (run 3) and *n*-butyl acrylate (run 4), respectively. In both runs, polymer molecular weight increases almost linearly with the increase of monomer conversion, demonstrating well-controlled "living" polymerization behavior. Therefore, the length of PS or PBA block in the block copolymers can be conveniently tuned by controlling the polymerization time, i.e., monomer conversion. On the basis of the GPC elution curves shown in Figures 8a and 9a, we can see that radical coupling is absent in both runs. However, slight broadening in molecular weight distribution is also seen in both runs with the increase of polymerization time, suggesting some possible deactivation/termination/transfer reactions. Regardless of this, the block copolymers generally possess narrow molecular weight distribution with PDI lower than 1.36 (at 10 h) and 1.25 (at 12 h) in runs 3 and 4, respectively.

The values of theoretical number-average molecular weight ($M_{\mathrm{n,theo}}$) of the four sets of block copolymers were also calculated by using the monomer conversion data and assuming uniform chain extension from each macroinitiator. The dependency of $M_{\mathrm{n,theo}}$ on monomer conversion for each set of block copolymers is shown in Figures 6b, 7b, 8b, and 9b, respectively. Obviously, the $M_{\mathrm{n,GPC}}$ values determined from GPC based on polystyrene are quite different from the $M_{\mathrm{n,theo}}$ values in each set. This is attributed to differences in hydrodynamic volumes between the block copolymers and polystyrene standards. The



	$M_{n,GPC}$ (kg/mol)	*PDI*
0 h	30.6	1.13
1 h	33.6	1.15
2 h	36.6	1.16
4 h	41.4	1.19
6 h	43.0	1.25
12 h	50.8	1.25

Figure 9. (a) Gel permeation chromatography elution traces and (b) number-average molecular weight (M_n) and polydispersity index (PDI) vs conversion for polyethylene-*b*-poly(*n*-butyl acrylate) block copolymers synthesized in the atom-transfer radical polymerization of *n*-butyl acrylate with PEMI-2 (run 4).

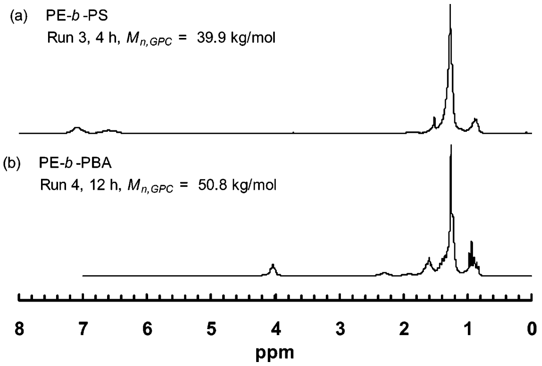


Figure 10. ^{1}H nuclear magnetic resonance spectrum of (a) polyethylene-*b*-polystyrene block copolymer synthesized in run 3 at 4 h and (b) polyethylene-*b*-poly(*n*-butyl acrylate) block copolymer synthesized in run 4 at 12 h.

structures of these diblock copolymers were analyzed using ^{1}H NMR spectroscopy. Representatively, Figure 10 illustrates the ^{1}H NMR spectra of two block copolymers synthesized from PEMI-2, PE-*b*-PS (4 h in run 3, $M_{n,GPC}$ = 39.9 kg/mol) and PE-*b*-PBA (12 h in run 4, $M_{n,GPC}$ = 50.8 kg/mol), respectively. The presence of both blocks derived from ethylene and the functional monomer (styrene or *n*-butyl acrylate) in the copolymers is clearly demonstrated.

The thermal properties of the two sets of block copolymers obtained from PEMI-2 in runs 3 and 4 were determined by DSC. The effect of the length of the functional monomer block on copolymer thermal properties was evaluated. Figures 11 and 12 compare the DSC thermograms of the two sets of block copolymers containing different length of the functional monomer block. For the purpose of comparison, the DSC thermogram for the PE macroinitiator, PEMI-2, is also shown on both figures. Because of its highly branched structure (85 branches/1000 C), PEMI-2 exhibits a melting endotherm at $T_m \approx -26.3$ °C with $\Delta H_m \approx 22.6$ J/g and a glass-transition temperature (T_g) at −64.6 °C. With the introduction of the functional monomer block of increasing length, a gradual change in the thermal properties of the block copolymers is found. A single glass transition is observed for the PE-*b*-PS copolymers synthesized in run 3 at 1 and 2 h as shown in Figure 11. However, the value of T_g (−60.7 and −61.2 °C, respectively) is significantly increased compared to that of the PEMI-2, showing the effect of the PS block. For the copolymers obtained at a longer polymerization time (4, 6, 10 h), i.e., having a longer PS block, two glass transitions (one at about −61 °C and the other at about 105 °C) are observed. These two glass transitions are attributed to the PE and PS blocks, respectively, and indicate the phase separation between the PE and PS blocks in these copolymers. Moreover, the glass transition at 105 °C becomes more obvious with the further increase of PS block length. For PE-*b*-PBA copolymers synthesized in run 4, similar phenomena are observed as shown in Figure 12. A second glass transition at about −48 °C, attributable to that of the PBA block, appears in the copolymers synthesized after 4 h of polymerization and the glass transition of the PE block is increased to about −61 °C. The melting endotherm of the PE block is still observed in both sets of block copolymers, and its peak position remains unaffected in the block copolymers, as shown in Figures 11 and 12.

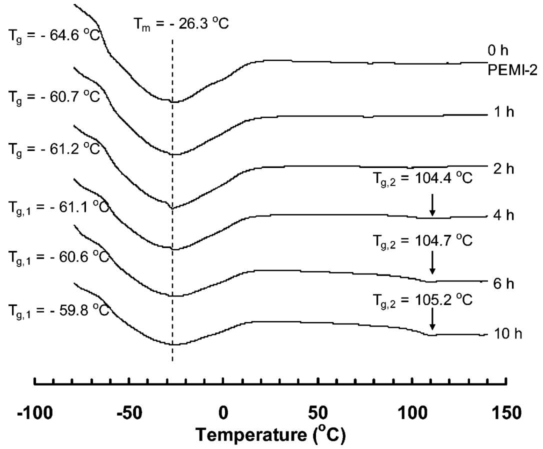


Figure 11. Differential scanning calorimetry thermograms for the set of polyethylene-*b*-polystyrene block copolymers synthesized in run 3 with PEMI-2 as the macroinitiator.

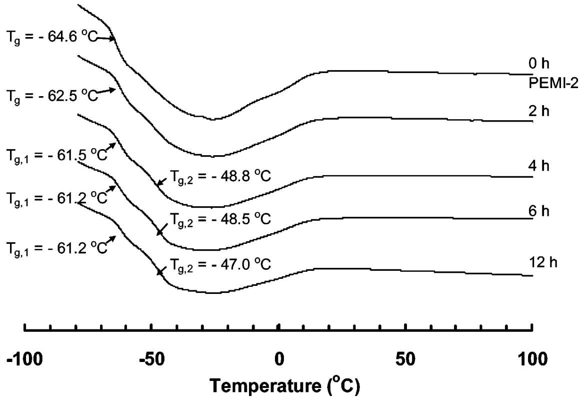


Figure 12. Differential scanning calorimetry thermograms for the set of polyethylene-*b*-poly(*n*-butyl acrylate) block copolymers synthesized in run 4 with PEMI-2 as the macroinitiator.

Conclusions

In this work we have demonstrated a novel two-step tandem synthetic strategy combining Pd−diimine catalyzed "living" ethylene polymerization and ATRP to synthesize well-defined functionalized PE block copolymers containing a PE block and a functional monomer (styrene or *n*-butyl acrylate) block. This strategy is enabled by developing a novel functionalized Pd−diimine catalyst, **3**, which was synthesized by reacting **1** with BIEA. The unique structure of this catalyst was confirmed using NMR and single-crystal XRD measurements. The catalyst initiates successfully ethylene "living" polymerization at 5 °C and an ethylene pressure of 400 psi, leading to narrow-distributed telechelic polyethylenes containing a terminal 2-bromoisobutyryl group. These telechelic PEs can thus be used as macroinitiators for subsequent ATRP. ATRPs of styrene and *n*-butyl acrylate were carried out using two PE macroinitiators of different chain lengths. Successful chain extensions were achieved from both initiators, and block copolymers having narrow polydispersity and a functional monomer block of controllable length were conveniently synthesized.

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Supporting Information Available: ^{13}C NMR spectra of **3** in CD_2Cl_2 and tables of crystallographic data, atomic coordinates, and isotropic thermal parameters, bond lengths and angles, anisotropic displacement parameters, H atom coordinates and isotropic displacement parameters, and torsion angles for complex **3**. This material is available free of charge via the Internet at http://pubs.acs.org.

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