Poly(ethylene-*co*-propylene macromonomer)s: Synthesis and Evidence for Starlike Conformations in Dilute Solution

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ABSTRACT: By use of two sequential coordination−insertion polymerizations, a series of ethylene-*co*-propylene-based comb polymers was synthesized. First, poly(ethylene-*co*-propylene) macromonomers featuring one unsaturated chain end were synthesized using a titanium bis(phenoxyimine) catalyst. The macromonomers were then homopolymerized using a living nickel α-diimine catalyst. The molecular weights and corresponding number of arms for each poly(macromonomer) were determined using size-exclusion chromatography with viscometry detection and universal calibration. Viscosity−molecular weight conformation plots for the poly(macromonomer)s revealed compact solution structures. Furthermore, viscometric radii for each poly(macromonomer) (R_v) and corresponding linear macromonomer $(R_v)_a$ were determined and the ratio $(R_v)/(R_v)_a$ for each pair was compared to those of a variety of polyisoprene-based star polymers with similar functionality. The comparison revealed that despite the obvious comb topology of the poly(macromonomer)s their dilute solution conformations correspond reasonably well to the bona fide polyisoprene stars.

Introduction

The ability to control polymer structure and molecular weight is among the most important facets of synthetic polymer chemistry, as these aspects ultimately dictate material properties.[1] This is particularly evident in the field of olefin polymerization. Research during the past several decades has brought forth transition-metal-based single site catalysts that offer exceptional control over the regio- and stereochemistry[2,3] of polymerization. Furthermore, the development of living catalysts[4,5] has established olefin polymerization that is devoid of chain termination events. Those catalysts that encompass both living behavior and the ability to control microstructure have facilitated the synthesis of new, well-defined polyolefin architectures including, most notably, block copolymers.[5]

Branching provides a means to radically alter the architecture and properties of basic linear polymers.[6−14] Methods for forming branched polymers can, for example, enable the covalent linkage of immiscible polymers, which can circumvent the macrophase separation that might occur with a traditional blend.[13,15] Beyond this, extensive research on the bulk and solution properties of branched systems has revealed other unique and potentially useful characteristics.[7,12,16−36] For example, it has been shown that the introduction of even a modest degree of long-chain branching can have a profound effect on the processability of a polymer.[33,37,38] This phenomenon has been extensively applied to isotactic polypropylene (*i*PP), a commodity thermoplastic whose U.S. sales in 2006 exceeded 18 billion pounds.[39] Significant efforts have been made to produce long-chain branched polymers that improve the processibility[31,34,38,40−42] and impact strength[43,44] of *i*PP because the poor melt strength of conventional linear *i*PP precludes its use in some manufacturing processes such as foaming or blow molding.[31,42]

Star polymers are one of the simplest type of branched macromolecules. They feature several linear chains that emanate from a central core; this core may be an atom, a small molecule, or a macromolecular structure.[11] Star polymers are typically formed by one of three general routes.[11] The "arm-first" approach involves the synthesis of living macromolecular chains which are coupled to a multifunctional linking agent, while the "core-first" approach involves a multifunctional compound which can simultaneously initiate the polymerization of several arms. In a third approach, a living polymer precursor can be combined with a difunctional monomer to form a cross-linked microgel, which functions as the core of a star. The synthesis of the first star polymer was reported by Schaefgen and Flory[45] in 1948. In their system, ϵ-caprolactam was polymerized in the presence of either a tetrabasic or octabasic carboxylic acid to produce tetra- and octachain polymers, respectively. In addition to the methods involving polycondensation, a multitude of polymerization techniques have been used for star synthesis including anionic,[46] cationic,[47,48] and nitroxide-mediated polymerization[49] as well as atom transfer radical polymerization (ATRP)[50] and ring-opening metathesis polymerization (ROMP).[11] Among these techniques, living anionic polymerization has been, perhaps, the most developed and exploited.[46] In particular, the linking of living anionic polymer chains to multifunctional electrophiles, such as chlorosilanes,[51] has been instrumental in producing model star polymers featuring up to 128 arms[52,53] due to the fact that substitution proceeds without side reactions. Living anionic polymerization has also been used in the formation of starlike polymers featuring a cross-linked microgel core.[46] This approach involves the reaction of a living anionic polymer chain with a difunctional monomer such as divinylbenzene[54] or ethylene glycol dimethacrylate (EGDM).[55] It has been used to form starlike polymers with arms based on polystyrene,[54,56] polystyrene-*b*-polydiene,[57] poly(alkyl methacrylate)s,[55] and combinations thereof.[58]

The homopolymerization of macromonomers[12] offers another method for the formation of starlike polymers. While these

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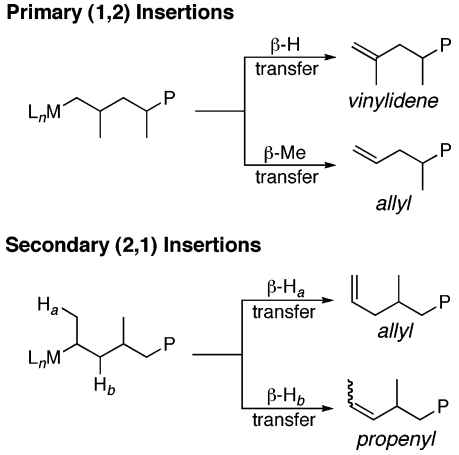
Scheme 1. Common Propylene Polymerization Chain-Transfer Pathways

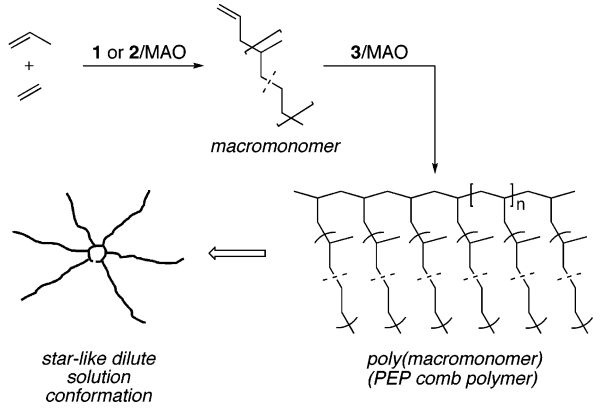


polymers are formally combs in that they feature branches that emanate from a linear backbone, they can adopt a variety of conformations in solution[12] (comblike, starlike, flowerlike, and bottle brush are common descriptors).[9,12] Factors such as the relative length of the backbone as compared to the side chains, the distance between branches,[29] and branch flexibility[9] determine the solution and bulk properties[19,24,27−30,35,36,59] of poly(macromonomer)s. In particular, the starlike distinction has commonly been given to poly(macromonomer)s based on combined observations from size-exclusion chromatography (SEC), viscosity measurements, and light scattering.[12]

Alongside a variety of other compositions, polyolefin-based macromonomers have been synthesized[12] and homopolymerized. In one example, Kaneko and co-workers,[60−62] radically homopolymerized methacryloyl-terminated poly(ethylene-*co*-propylene) that was formed from vinylidene-terminated poly(ethylene-*co*-propylene) made using Cp_2ZrCl_2/MAO (Cp = cyclopentadienyl, MAO = methylaluminoxane). In another example, Senoo and Endo[63] reported the homopolymerization of styrene-terminated polyisoprene using half-titanocene catalysts such as $CpTiCl_3$/MAO; here the macromonomer was formed by the reaction of the living anionic chain end of polyisoprene with *p*-chloromethylstyrene. In these examples, coordination−insertion polymerization has been used either in the formation of a macromonomer or in the homopolymerization of a macromonomer. To our knowledge, there are no examples of using coordination−insertion polymerization for both steps, a system that could provide all aliphatic hydrocarbon-based starlike polymers without the need for macromonomer end-group elaboration. This would require both a catalyst capable of producing polyolefins with olefinic end groups suitable for polymerization (but one that does not readily polymerize these macromonomers in situ) and a catalyst capable of the polymerization of these macromonomers.

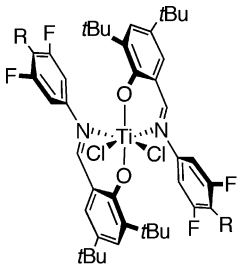
The reactivity of an alkene-terminated polyolefin toward coordination−insertion polymerization should increase as the steric congestion about its olefin end group decreases. The synthesis of vinyl-terminated polyethylene is straightforward as the vinyl end group is the only type that can be formed via β-hydride (β-H) transfer. However, the polymerization of propylene typically occurs through a 1,2-insertion mechanism and β-H transfer yields a sterically congested vinylidene end group (see Scheme 1).[64−66] Polypropylene featuring a sterically less-encumbered allyl end group can be formed either by using catalysts that exhibit a 1,2-insertion mechanism but favor β-Me elimination[65,67−70] over β-H transfer or by using catalysts that exhibit a 2,1-insertion mechanism and favor β-H transfer. As an example of the latter, iron pyridine bis-imine[71,72] complexes/

Scheme 2. Two Step Synthesis of Poly(ethylene-*co*-propylene)-Based Poly(macromonomer)s

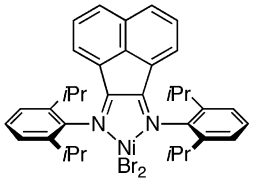


MAO polymerize propylene via a 2,1-insertion mechanism and provide iso-enriched allyl-terminated polypropylene.[73,74] Additionally, titanium bis(phenoxyimine) complexes such as **1** and **2**, when activated with MAO, also polymerize propylene in a 2,1 fashion but form syndio-enriched to highly syndiotactic allyl-terminated polypropylenes.[75−79]

The best candidates for the homopolymerization of these vinyl- or allyl-terminated polyolefins are those that are active for the polymerization of relatively bulky monomers, such as higher α-olefins. A living catalyst is also desired to ensure a narrow molecular weight distribution for the poly(macromonomer)s. Fortunately, several catalysts that are both active for higher α-olefin polymerization and living have been developed in recent years.[80−82]



1 R = F
2 R = H



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Herein, we report the synthesis and characterization of a series of olefin-based poly(macromonomer)s. This was accomplished by first synthesizing poly(ethylene-*co*-propylene) (PEP) samples featuring unsaturated end groups using titanium bis(phenoxyimine) complexes **1** and **2** with MAO (Scheme 2) and then using nickel α-diimine complex **3**/MAO to carry out the subsequent homopolymerizations. The resulting poly(macromonomer)s are, nominally, comb polymers whose arms are very closely spaced. SEC viscometry detection with universal calibration was used to measure the absolute molecular weight distributions of the polymers, to determine the functionalities (number of arms) of the poly(macromonomer)s, and to study their solution properties. As will be shown later, the solution conformations of the poly(macromonomer)s correspond reasonably well to those of polyisoprene-based star polymers prepared using chlorosilane linking of anionically polymerized arms.

PEP is an amorphous, low T_g material that has a relatively low entanglement molecular weight ($M_e \sim 1{,}300-1{,}800$ g/mol)[83] and consequently is an attractive material for a variety of industrial applications such as isotactic polypropylene impact strength modification[84,85] and oil viscosity improvement.[86−88] Given the potential and realized applications of poly(mac-

romonomer)s including use as emulsifiers, polymer blend compatibilizers,[89] and modifiers for paints, coatings, adhesives, and films,[9] highly branched PEP-based materials such as those described herein could prove to be interesting and potentially useful.

Experimental Section

General. All manipulations of air- and/or water-sensitive compounds were carried out under dry nitrogen using a Braun UniLab drybox or standard Schlenk techniques. Toluene was purified over columns of alumina and copper (Q5). Propylene (Matheson, polymer grade) was purified over columns of molecular sieves and copper (Q5). Ethylene (Matheson, polymer grade) was purified by passing it through an Oxiclear model DGP-250-R2 purification column. PMAO-IP (13 wt % Al in toluene, Akzo Nobel) was dried in vacuo to remove residual trimethylaluminum and used as a solid white powder. MMAO-7 (7.1 wt % Al in Isopar E, Akzo Nobel) was used as received.

Polymer Characterization. ^{1}H NMR spectra of the polymers were recorded on a Varian INOVA (500 MHz) spectrometer equipped with a ^{1}H/BB switchable probehead with single axis pulse field gradient and were referenced versus residual non-deuterated solvent shifts. The polymer samples were dissolved in benzene-d_6 in a 5 mm o.d. tube, and spectra were collected at room temperature.

Macromonomer End-Group Analysis via NMR Spectroscopy. The ^{13}C NMR spectrum was recorded on a Varian INOVA 600 spectrometer operating at 150.828 MHz for ^{13}C observation using a 10 mm broad-band direct observe probehead. The spectrum was acquired observing a ^{13}C chemical shift range from 172 to 7 ppm with an acquisition time of 1.3 s and d1 relaxation delay of 0 s using 67.5 degree pulses and broad-band ^{1}H decoupling. 39,000 scans were averaged for a total acquisition time of 14.1 h. The spectrum was zero filled to 128K complex points and an unshifted Gaussian window was applied prior to Fourier transformation. ^{13}C chemical shifts were referenced to the residual non-deuterated solvent peak. The gradient selected HMBC spectrum was recorded on a Varian INOVA 600 spectrometer operating at 599.757 MHz for ^{1}H observation using a Varian inverse ^{1}H-{^{13}C,^{15}N} triple-resonance probehead with triple-axis gradients. The spectrum was acquired in absolute value mode with sweep widths of 5.1 and 36.2 kHz in ^{1}H and ^{13}C dimensions, respectively. A total of 1000 points were collected in the indirectly detected dimension with 8 scans and 2K points per increment. The resulting matrix was zero filled to 2K × 4K complex data points, and a 30°-shifted sinusoidal window function was applied in t_2 dimension prior to Fourier transformation.

Fractionation Progress Assessment. The purification of poly(macromonomer)s was monitored by SEC in 1,2,4-trichlorobezene containing 0.01 wt. % di-*tert*-butylhydroxytoluene (BHT) at 1.0 mL/min at 140 °C with a Waters Alliance GPCV 2000 GPC equipped with a Waters DRI detector and viscometer and a column set consisting of four Waters HT 6E and one Waters HT 2. The poly(macromonomer)s are readily soluble in several organic solvents at room temperature. High-temperature SEC was employed here because it was conveniently available at the time of purifications.

Size Exclusion Chromatography (SEC). Absolute molecular weights and polymer solution properties of macromonomers and purified poly(macromonomer)s were measured in uninhibited HPLC-grade THF at 35 °C with three Varian, Inc. Plgel mixed-C 7.8 × 300 mm columns. Instrumentation consisted of a Waters Corporation 2695 solvent delivery and sample management module, a Waters 2487 dual wavelength spectrophotometric (UV) detector, a Precision Detectors PD2020 two-angle light scattering detector, a Waters 410 differential refractive index (DRI) detector, and a Viscotek H502A differential viscometer. The spectrophotometric and light scattering detectors were connected in series after the columns, and the viscometer was connected with a parallel split to the DRI detector after the light scattering detector. Flowrates were nominally 1.0 mL/min. Samples contained 0.2% acetone as a flow marker, and all injection volumes were 100 μL. Sample concentrations were 2 and 3 mg/mL for macromonomers and poly(macromonomer)s, respectively. A universal calibration curve[90] was constructed from *n*-phenylhexane and 15 narrow-distribution Varian, Inc. polystyrene standards with known intrinsic viscosities between molecular weights 580 and 1,920,000. Absolute molecular weight distributions were calculated from the differential viscometry detector response combined with the universal calibration curve. The weight-average molecular weights were confirmed by SEC light scattering detection using a specific refractive index increment (d*n*/d*c*) of 0.078 mL/g for the poly(macromonomer)s in THF.

Complex Synthesis. Bis(2,4-di-*tert*-butyl-6-[(3,4,5-trifluorophenylimino)methyl]phenolato)titanium dichloride (**1**) and Bis(2,4-di-*tert*-butyl-6-[(3,5-difluorophenylimino)methyl]phenolato)titanium dichloride (**2**) were prepared similarly to a previously reported method.[91] (ArN═C(1,8-naphthalenediyl)C═NAr)$NiBr_2$ (Ar = 2,6-diisopropylphenyl) (**3**) was also prepared by a previously reported method.[92]

Macromonomer Synthesis. Macromonomer batches (MM-1−MM-4) are comprised of the polymer produced from multiple polymerizations run under identical conditions. All individual polymerization runs were performed in a 12 oz Lab-Crest reaction vessel (Andrews Glass). In some cases, the flow of ethylene was metered using a Whitey metering valve with a vernier scale. After the reaction mixtures were quenched with 10 mL of methanol, they were poured into copious amounts of methanol/HCl and the resulting suspensions were allowed to stir for 12 h. The polymers were then isolated, rinsed with methanol, and dried in vacuo at 60 °C for at least 12 h. Each macromonomer batch was purified by dissolving the polymer in hot toluene, filtering the solution through a frit layered with celite, alumina, and silica gel, and then slowly dripping the resulting filtrate into copious amounts of methanol. The reprecipitated polymer was then isolated and dried in vacuo at 60 °C for several days.

MM-1. A solution of PMAO-IP (0.52 g, 9.0 mmol) in toluene (200 mL) was cooled to 0 °C and stirred under 30 psi propylene for 30 min. A solution of **1** (0.051 g, 60 μmol) in 5 mL toluene was injected, and an overpressure of 32 psi ethylene metered to 1.00 was applied. The reaction was quenched after 4 h. This was repeated four times for a total polymer yield of 74.6 g after purification.

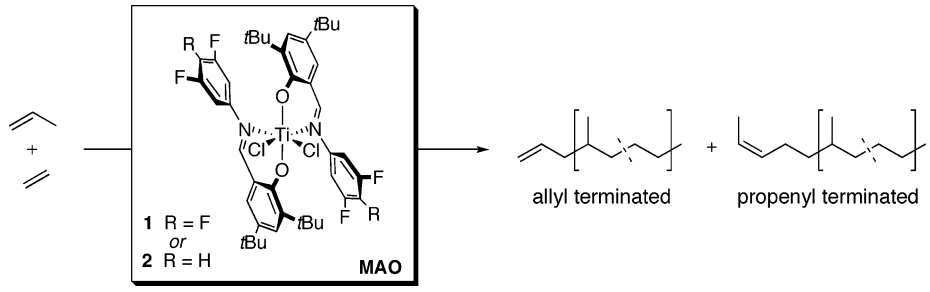
MM-2. A solution of PMAO-IP (0.52 g, 9.0 mmol) in toluene (200 mL) was cooled to 0 °C and stirred under 30 psi propylene for 30 min. A solution of **2** (0.048 g, 59 μmol) in 10 mL toluene was injected, and an overpressure of 32 psi ethylene metered to 1.01 was applied. The reaction was quenched after 4 h. This was repeated seven times for a total polymer yield of 152.9 g after purification.

MM-3. A solution of PMAO-IP (0.22 g, 3.8 mmol) in toluene (200 mL) was cooled to 0 °C and stirred under 30 psi propylene for 30 min. A solution of **2** (0.010 g, 13 μmol) in 5 mL toluene was injected and an overpressure of 32 psi ethylene metered to 1.02 was applied. The reaction was quenched after 3 h. This was repeated three times for a total polymer yield of 49.0 g after purification.

MM-4. A solution of PMAO-IP (0.22 g, 3.8 mmol) in toluene (200 mL) was cooled to 0 °C and stirred under 30 psi propylene for 20 min. A solution of **2** (0.010 g, 13 μmol) in 5 mL toluene was injected and an overpressure of 32 psi ethylene was applied. The reaction was quenched after 2.3 h. This was repeated four times for a total polymer yield of 55.3 g after purification.

Poly(macromonomer)s. Homopolymerization of each macromonomer batch is described below. Each reaction was quenched with methanol, after which the reaction mixture was poured into copious amounts of methanol/HCl. The resulting suspensions were allowed to stir for 12 h, after which the polymers were isolated, rinsed with methanol, and dried in vacuo at 60 °C for at least 12 h. Purification of each crude sample was carried out by fractional precipitation. Methanol was added slowly to stirred solutions of each crude poly(macromonomer) in diethyl ether. When the solution appeared cloudy, stirring was ceased and the precipitated polymer was allowed to settle overnight. The supernatant was decanted off, and the precipitated polymer was rinsed several times with a diethylether/methanol mixture, after which it was dried at 60 °C in

Scheme 3. Formation of PEP Macromonomer Using a Bis(phenoxyimine)titanium Dichloride Complex/MAO



vacuo for 12 h. This process was repeated several times with progress being measured by SEC.

PMM-1. Toluene (45 mL), MMAO-7 solution (30 mL, 57 mmol), and MM-1 (40.0 g as a solution in 200 mL toluene) were combined in a 500 mL Schlenk-adapted round-bottom flask under nitrogen. After the mixture was stirred for 5 min, a suspension of **3** (0.165 g, 0.229 mmol) in 30 mL toluene was added, and the resulting dark purple solution was cooled to 0 °C. The polymerization was quenched after 48 h.

PMM-2. Toluene (50 mL), MMAO-7 solution (30 mL, 57 mmol), and MM-2 (34.0 g as a solution in 200 mL toluene) were combined in a 500 mL Schlenk-adapted round-bottom flask under nitrogen. After the mixture was stirred for 5 min, a suspension of **3** (0.165 g, 0.229 mmol) in 30 mL toluene was added, and the resulting dark purple solution was cooled to 0 °C. The polymerization was quenched after 48 h.

PMM-3. Toluene (450 mL) and MM-3 (48.3 g) were combined in a 1 L round-bottom flask and allowed to stir overnight under nitrogen. To this solution was added MMAO-7 solution (44 mL, 84 mmol). After the mixture was stirred for 5 min, a suspension of **3** (0.118 g, 0.164 mmol) in 15 mL toluene was added, and the resulting dark purple solution was cooled to 0 °C. The polymerization was quenched after 72 h.

PMM-4. Toluene (450 mL) and MM-4 (49.7 g) were combined in a 1 L round-bottom flask and allowed to stir overnight under nitrogen. To this solution was added MMAO-7 solution (38 mL, 73 mmol). After the mixture was stirred for 5 min, a suspension of **3** (0.101 g, 0.141 mmol) in 15 mL toluene was added, and the resulting dark purple solution was cooled to 0 °C. The polymerization was quenched after 68 h.

Discussion

Synthesis of Poly(ethylene-*co*-propylene) Macromonomers. It has been previously reported that titanium bis(phenoxyimine) complexes **1**, **2,** and other related complexes produce highly syndiotactic, low molecular weight polypropylene upon activation with MAO.[79] These catalysts polymerize propylene via a 2,1-insertion mechanism[75,76] resulting in a relatively bulky metal-polymeryl species from which a β-H transfer could conceivably yield either a propenyl or an allyl end group (Scheme 1). However, polypropylenes made using these catalysts exclusively exhibit the latter providing a polymer with a sterically uncongested terminal olefin at one end. We questioned if copolymerizing ethylene and propylene with titanium bis(phenoxyimine) catalysts could provide predominantly allyl-terminated poly(ethylene-*co*-propylene)s (materials that would be suitable as amorphous, low T_g macromonomers with relatively low entanglement molecular weights). It should be noted that the synthesis of EP macromonomers has been previously reported by Zhu and co-workers[93,94] using the constrained geometry catalyst, [C_5Me_4($SiMe_2$N-*tert*-butyl)]-$TiMe_2$, activated with tris(pentafluorophenyl)boron and MMAO. The copolymerization of ethylene and propylene using this catalyst yielded a PEP macromonomer with M_n = 4100 g/mol. However, the portion of macromonomer suitable for polymerization was fairly low as the terminal unsaturation of the polymer was determined to be 38% vinyl and 31% vinylidene.[94]

Initial copolymerization studies were conducted using **2**/MAO (see Scheme 3). This catalyst produced low molecular weight ethylene−propylene copolymers as desired. However, a mixture of unsaturated end groups was present as evidenced from ^{1}H NMR. Resonances consistent with both allyl and propenyl end groups were present. While somewhat disappointing, this result was not unexpected given the fact that a mixture of monomers can result in the presence of a variety of metal chain-end structures from which a variety of unsaturated end groups can theoretically be formed via β-H transfer. Scheme 4 depicts examples of hypothetical ultimate and penultimate enchainments followed by chain termination via β-H transfer. It is expected that a portion of the allyl-terminated end groups that are present arise from β-H transfer after sequential 2,1-insertions of propylene, as in the case with propylene homopolymerization (see Scheme 4 inset). While it also seems possible that β-H transfer following an ethylene and then 2,1-propylene insertion sequence could also provide an allyl end group, the sterically more open metal chain-end species in this case could allow for β-H transfer from the methylene (rather than methyl) β carbon which would result in the formation of a propenyl end group. In another hypothetical example, propylene and then ethylene insertion precedes β-H transfer, which could result in the formation of a vinyl end group.

Taking into consideration two additional mechanistic aspects, the number of possible unsaturated end groups in these polymers and the routes by which they are formed can be increased. First, it has been shown by Hustad et al. that in ethylene−propylene copolymerizations using structurally related but living titanium bis(phenoxyimine) catalysts propylene can insert in either a 2,1 or a 1,2 fashion after a 1,2 propylene or ethylene insertion.[76,77] This provides a larger variety of chain ends from which β-H transfer can occur and hence provides a larger variety of possible end groups. Second, Cherian et al.[79] suggested that chain termination in this system occurs via β-H transfer to monomer rather than to metal. Here, it was demonstrated that the polymer molecular weight is independent of the initial propylene concentration, indicating that the β-H transfer has an order in monomer. Knowing this, one could propose that end-group formation becomes more complicated upon moving from propylene homopolymerization to ethylene−propylene copolymerization not solely because of the generation of sterically less-congested metal-chain species but perhaps also because of ethylene being better poised sterically than propylene to participate in the β-H transfer reactions.

The structures of the unsaturated end groups in these macromonomers were further probed by ^{13}C NMR spectroscopy (see Supporting Information). A long-duration ^{13}C{^{1}H} NMR experiment was first conducted on a representative sample, and the chemical shifts of resonances in the olefin region were compared to those of literature values[95] for a series of small molecules that mimic the postulated unsaturated end groups. A ^{1}H−^{13}C heteronuclear multiple-bond correlation (HMBC) experiment was also conducted on this polymer. The results from

Scheme 4. Examples of Possible Unsaturated End Groups Formed during Ethylene−Propylene Copolymerization Using 1 or 2 with MAO

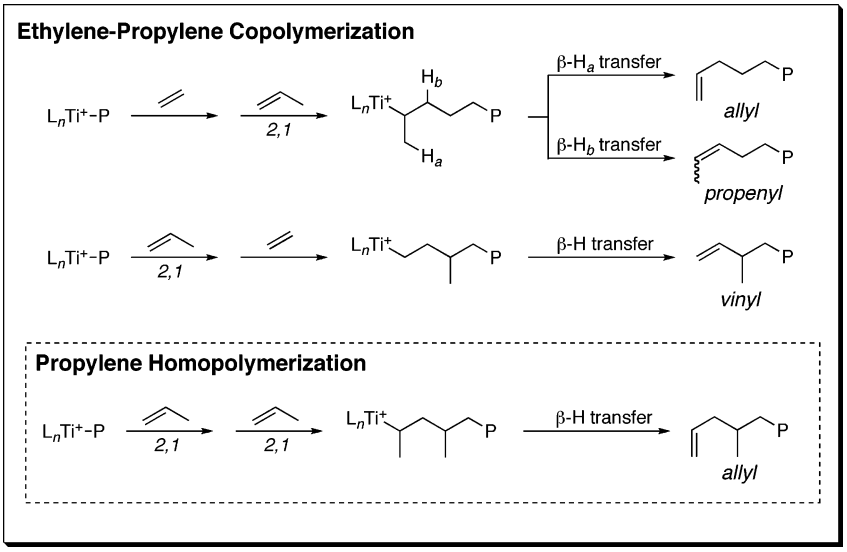


Table 1. PEP Macromonomer Characterization

sample	complex used	M_n (^{1}H NMR) (g/mol)	M_n (SEC, g/mol)	M_p[a] (SEC, g/mol)	[η] (dL/g)	M_w/M_n	M_z/M_w	mol % ethylene[b]	unsaturated end groups [allyl]:[propenyl][b]	T_g[c] (°C)
MM-1	**1**	4800	6910	11 500	0.195	1.62	1.41	29	65:35	−45.6
MM-2	**2**	8900	10 400	18 400	0.316	1.81	1.40	39	60:40	−50.6
MM-3	**2**	18 900	21 500	35 300	0.590	1.70	1.43	61	43:57	−62.3
MM-4	**2**	23 300	24 900	39 000	0.649	1.66	1.43	64	42:58	−61.2

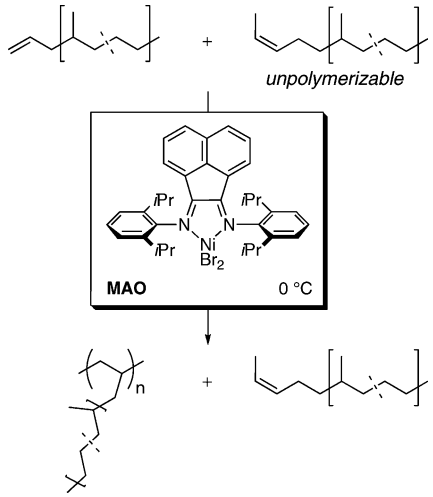
[a] Molecular weight at the peak apex of the differential weight fraction molecular weight distribution. [b] Determined via ^{1}H NMR. [c] Determined by DSC (second heat).

these two experiments showed that the sample indeed contains a complex mixture of unsaturated end groups but confirmed the presence of the expected allyl end group and the absence of the proposed vinyl end group (see Scheme 4). The data also revealed that all propenyl end groups are present in the cis configuration.

While there are a variety of end-group structures in these polymers, of principal concern is the portion of chains that bear an end group suitable for subsequent homopolymerization. Chains featuring an allyl end group are considered polymerizable, while those featuring an internal olefin are considered to be essentially unpolymerizable (vide infra). To this end, ^{1}H NMR spectroscopy provides a reasonable estimate of the ratio of allyl-terminated (polymerizable) to propenyl-terminated (unpolymerizable) chains.

Table 1 summarizes the characterization of four poly(ethylene-*co*-propylene) macromonomer batches (MM-1−MM-4**)** synthesized by using either **1**/MAO or **2**/MAO. Fortunately, the molecular weights of poly(ethylene-*co*-propylene)s formed using these catalysts were higher relative to their corresponding propylene homopolymerizations; at 0 °C, **1**/MAO produces polypropylene with $M_n \sim 3100$ g/mol while **2**/MAO produces polypropylene with $M_n \sim 5700$ g/mol. This enabled the synthesis of a series of PEP macromonomers with a variety of molecular weights. End-group analysis via ^{1}H NMR spectroscopy as well as SEC with universal calibration was used to determine M_n values for each macromonomer and, as shown, the values compare reasonably well. Other molecular weight averages were also determined from the SEC molecular weight distributions. As expected, the polydispersities (M_w/M_n) approach a value of 2 in each case. Unfortunately, as the molecular weight of the macromonomers increase, so too does ethylene content. Because of this, molecular weight and ethylene content cannot be independently varied. Furthermore, the portion of macromonomer chains featuring unpolymerizable end groups also increases with increased molecular weight/ethylene content, which results in inherently reduced yields for the subsequent macromonomer homopolymerizations.

Scheme 5. Homopolymerization of Macromonomer with 3/MAO



The use of both **1** and **2** was necessary to produce the desired series. The lowest targeted molecular weight was $M_n \sim 4500$ g/mol which precluded the use of **2**/MAO. While **1**/MAO could have theoretically been used exclusively for the entire series, higher amounts of ethylene incorporation would have been necessary to achieve the same given molecular weight using **2**/MAO. This would be undesirable because the mole fraction of propenyl (unpolymerizable) end groups increases with increased ethylene incorporation. In addition, sufficiently high ethylene content could lead to the onset of crystallinity.

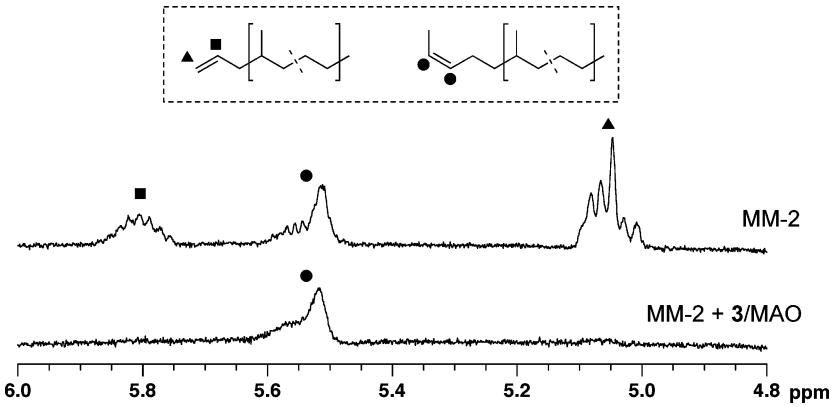


Figure 1. ^{1}H NMR spectra of MM-2 and MM-2 + **3**/MAO.

One potential complication of the macromonomer synthesis is the reincorporation of the macromonomer into subsequently formed chains. To evaluate the feasibility of this, the polymerization of MM-2 was repeated with the addition of 4-methyl-1-pentene, a model for allyl-terminated macromonomer. Additionally, the repeat unit of poly(4-methyl-1-pentene) features two homotopic carbons, and the chemical shift (23.5 ppm) of these carbons falls within a region devoid of resonances in the ^{13}C NMR spectrum of MM-2. For the polymer produced, no peak indicative of 4-methyl-1-pentene incorporation was present in the ^{13}C NMR spectrum. This suggests that the PEP macromonomer formed by **2**/MAO is too bulky to be polymerized by that catalyst and therefore in situ macromonomer incorporation is not likely operative.

Homopolymerization of Poly(ethylene-*co*-propylene) Macromonomers. Complex **3**/MAO was chosen as a catalyst for the homopolymerization of the macromonomers. This catalyst was originally reported by Brookhart and co-workers in 1995 to be active for the polymerization of ethylene, propylene, and 1-hexene,[92] and in 1996, it was shown to be living for the polymerization of propylene, 1-hexene, and 1-octadecene.[82] Interestingly, it was later reported that **3**/MAO could polymerize *trans*-2-butene to form a 1,3-enchained polymer.[96] The catalyst is far less active for *cis*-2-butene polymerization,[97] but when employing a mixture of the two monomers, the presence of the cis isomer appears not to inhibit the polymerization of the trans isomer. In the polymerizations studied here, if one views the allyl-terminated macromonomer as being akin to a higher α-olefin, such as 1-hexene, and views the propenyl-terminated macromonomer as being akin to *cis*-2-butene, then it is reasonable to expect the activity of allyl-terminated macromonomer polymerization to far exceed that of the propenyl-terminated macromonomer polymerization. Furthermore, the presence of the propenyl-terminated macromonomer is not expected to inhibit the homopolymerization. In addition to **3**/MAO being a promising choice for a homopolymerization catalyst based on the nature of the monomers used herein, the relatively low oxophilicity of this class of catalyst and the ability to use a large excess of MAO as a cocatalyst are desirable as very rigorous purification of the macromonomers is not feasible.

Each macromonomer batch was homopolymerized using **3**/MAO at 0 °C over 2−3 days (see Scheme 5). SEC was used to analyze the crude poly(macromonomer) samples. In each chromatogram, the presence of unreacted macromonomer as well as a higher molecular weight peak was evident. In addition, Figure 1 shows a region of the ^{1}H NMR spectra for MM-2 and the crude polymer obtained from its homopolymerization with **3**/MAO (MM-2 + **3**/MAO). In the spectrum for the crude poly(macromonomer), only very weak resonances can be seen at approximately 5.80 and 5.05 ppm compared to the peak at approximately 5.50 ppm. This indicates a strong preference for the incorporation of the allyl- rather than the propenyl-terminated macromonomer. Each crude poly(macromonomer) was subjected to repeated fractional precipitations (the progress of which was assessed by SEC) in an attempt to remove the residual macromonomer. Relatively pure poly(macromonomer)s (PMM-1−PMM-4) were isolated with approximately 4, 11, 10, and 13 wt % residual macromonomer, respectively.

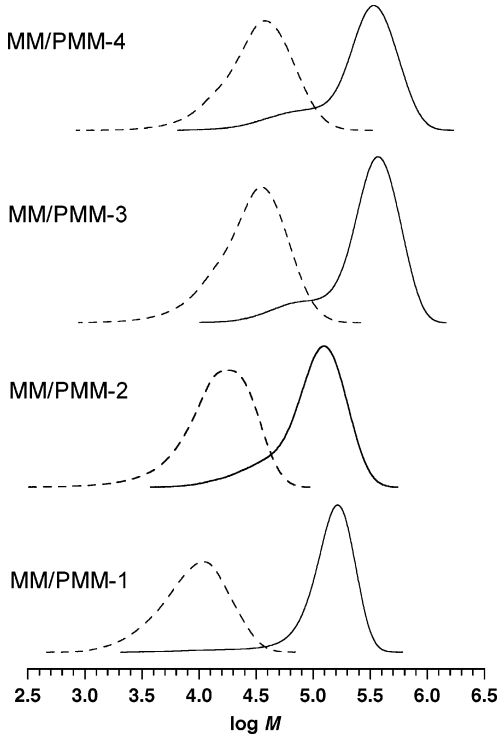


Figure 2. SEC chromatograms of the macromonomers (broken line) and the corresponding poly(macromonomer)s (solid line).

Number-average molecular weights and polydispersity indices M_w/M_n and M_z/M_w reported in Table 2 were determined by SEC (viscometry detection and universal calibration). The data on number of arms $f(M_n)$ calculated from the number-average molecular weights of the macromonomers and their polymerized products are also provided in Table 2. However, the presence of low molecular weight material (i.e., 4−13% residual macromonomer) in the poly(macromonomer) samples can significantly affect the M_n values, which in turn introduces uncertainty in the calculation of $f(M_n)$. The number of arms calculated from the peak molecular weights, $f(M_p)$, is affected less by the residual

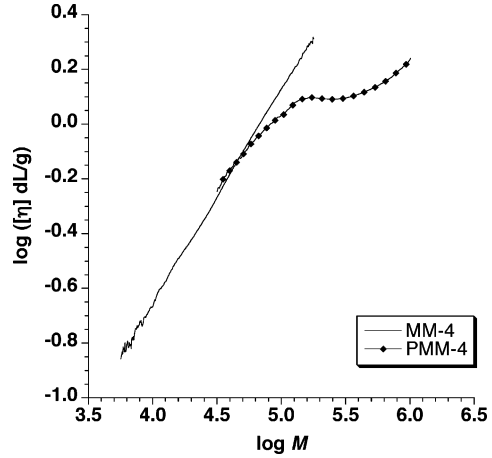


Figure 3. Representative conformation plots for MM-4 and PMM-4.

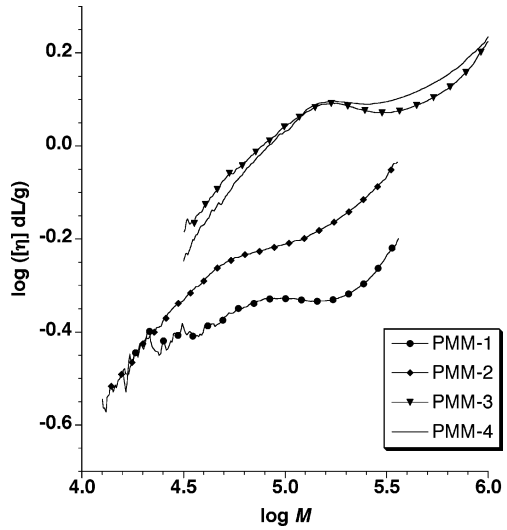


Figure 4. Conformation plots for PMM-1 through PMM-4.

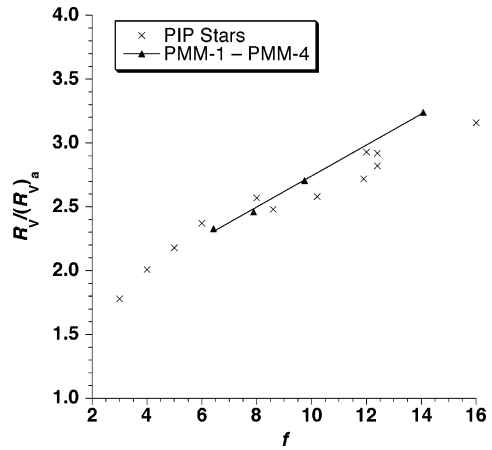


Figure 5. $R_v/(R_v)_a$ versus f for PMM-1 through PMM-4 and PIP star samples from Bauer et al.[17]

macromonomer and is likely to provide a more accurate estimate of f. The values are in fair agreement with the theoretical values (f_{theor}) calculated from the moles of polymerizable macromonomer (based on M_n (SEC)) and the moles of catalyst used in each homopolymerization, assuming complete consumption. Given that these polymerizations should be living, one would expect a narrowing of the molecular weight distribution upon going from macromonomer to poly(macromonomer) as is the case when polymeric arms are completely linked into stars.[10,45] However, the polydispersities narrow only slightly upon going from the macromonomers to the corresponding poly(macromonomer)s in most cases, and the M_w/M_n PDI of PMM-4 is actually higher than that of MM-4 (1.90 vs 1.66). This again is explained by the presence of residual macromonomer. Values for M_z/M_w given in Table 2 provide another measure of the polydispersity of the poly(macromonomer)s that does not depend on the anomalously low M_n values. The M_z/M_w value does in fact decrease upon going from the macromonomer to the corresponding poly(macromonomer) in each case. Moreover, Figure 2 provides the SEC chromatograms for the macromonomer and macromonomer-purified poly(macromonomer) pairs, and the difference in the breadth of the two peaks of each pair is clearly seen.

Solution Properties of the Poly(macromonomer)s. The viscosity−molecular weight conformation plot for MM-4 in Figure 3 exhibits simple power-law behavior that can be described by the empirical Mark−Houwink−Sakurada relationship and is representative of linear polymer. PMM-4 is a mixture of poly(macromonomer) and linear macromonomer, resulting in a nonlinear conformation plot. The viscosity of PMM-4 coincides with that of the residual MM-4 at low molecular weights. At higher molecular weights, the poly(macromonomer) fraction of the sample has lower intrinsic viscosity than its constituent macromonomer, which is an expected consequence of greater mass per unit contour length. As with PMM-4, each of the other three samples exhibits a transition in viscosity upon moving from the low molecular weight linear macromonomer to the high molecular weight poly(macromonomer) regimes (Figure 4). Furthermore, as expected, the intrinsic viscosity of each poly(macromonomer) at a given molecular weight in the high molecular weight region increases as the constituent arm length increases, i.e., the structures are less compact as the incorporated macromonomer arm lengths increase.

A qualitative observation from the conformation plots is that the slopes of the poly(macromonomer)s in the high molecular weight regions of the plots are nearly parallel but are offset to the linear macromonomer plots. Star polymer conformation plots look similar, i.e., the Mark−Houwink−Sakurada scaling exponent of a star polymer is the same as the constituent linear arms and the offset is proportional to the number of arms. This leads us to examine the poly(macromonomer) structures as if they are starlike, as depicted in Scheme 2, using the viscometric radius ratio of the starlike polymer to that of an individual arm.

In 1989, Fetters and co-workers[17] reported the measurement of chain dimensions using viscometry and light scattering for a series of polyisoprene (PIP) stars of varying functionality. These stars were prepared using chlorosilane linking of anionically polymerized arms (vide supra). One part of this study involved the determination of viscometric radii (R_v) for the stars and the constituent arms according to eq 1

$$R_v = \left(\frac{3M[\eta]}{10\pi N_A}\right)^{1/3} \quad (1)$$

where N_A is Avogadro's Number. For each star, the ratio of R_v to $(R_v)_a$, the viscometric radius of the corresponding arm, was determined. In Figure 5, $R_v/(R_v)_a$ versus f is plotted for some of these PIP stars (where $3 \leq f \leq 16$) under good solvent conditions. Together with these are plotted the analogous data for the PEP poly(macromonomer)s. These values were determined using eq 1 for R_v (where $M = M_w$) and f values based on M_w, i.e., $f(M_w)$, to be consistent with results reported in ref 17. The plots indicate that despite the obvious comb topology

Table 2. Poly(macromonomer) Characterization

sample	M_n (SEC, g/mol)	M_p[a] (SEC, g/mol)	$[\eta]$ (dL/g)	M_w/M_n	M_z/M_w	$f(M_n)$	$f(M_p)$	f_{theor}[b]
PMM-1	104 500	166 000	0.471	1.51	1.17	15.1	14.4	16
PMM-2	74 000	125 500	0.623	1.62	1.31	7.1	6.8	9
PMM-3	209 000	371 000	1.119	1.70	1.29	9.7	10.5	6
PMM-4	172 000	343 000	1.224	1.90	1.35	6.9	8.8	6

[a] Molecular weight at the peak apex of the differential weight fraction molecular weight distribution. [b] Calculated by the equation [initial grams of allyl-terminated macromonomer/M_n (SEC) macromonomer (g/mol)]/[no. of moles of **3**], assuming complete consumption of polymerizable macromonomer.

of these polymers their solution conformations correspond reasonably well to those of the bona fide star polymers of similar functionality, a consequence of short contour lengths and comparatively long arms as reported previously by Tsukahara et al.[19]

Conclusions

We have reported a route to all-aliphatic hydrocarbon-based comb polymers via sequential coordination−insertion polymerizations. Ethylene-*co*-propylene was chosen as the base polymer for these long-chain branched polyolefins because its properties (lack of crystallinity, low T_g, and low M_e) make it an attractive polymer for a variety of applications. Titanium bis(phenoxyimine) complexes **1** and **2** with MAO provided an effective means of producing macromonomer with a reasonable portion of allyl (polymerizable) end groups. In each case, the nickel α-diimine complex **3**/MAO was effective for macromonomer homopolymerization and yielded high molecular weight species. Each crude poly(macromonomer) was subjected to fractional precipitation which resulted in the isolation of relatively pure poly(macromonomer) (4−13% residual macromonomer). Analysis of the poly(macromonomer) series by SEC revealed that they featured between ∼6.8 and 14.4 arms/molecule, on average, based on M_p values; these values correspond reasonably well to the theoretical values based on reaction stoichiometry. SEC was also used to probe the solution properties of the poly(macromonomer)s. Viscosity−molecular weight conformation plots revealed that the poly(macromonomer)s have compact solution structures, and furthermore the compactness decreases with increasing arm length through the series. The viscometric radii provided a useful means to compare the chain dimensions of these poly(macromonomer)s to those of the PIP star polymers. Good agreement between $(R_v)/(R_v)_a$ values for the poly(macromonomer)s reported herein and those for the PIP star polymers was found. While these PEP poly(macromonomer)s are nominally considered combs, this result suggests that they may possess starlike conformations in dilute solution.

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Supporting Information Available: Details of macromonomer end-group analysis by NMR spectroscopy including $^{13}C\{^1H\}$ and $^1H-^{13}C$ HMBC experiments. This material is available free of charge via the Internet at http://pubs.acs.org.

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