Synthesis and Characterization of Alternating and Multiblock Copolymers from Ethylene and Cyclopentene

Masayuki Fujita and Geoffrey W. Coates*

Department of Chemistry and Chemical Biology, Baker Laboratory, Cornell University, Ithaca, New York 14853-1301

Received August 19, 2002

ABSTRACT: The synthesis and characterization of copolymers from ethylene and cyclopentene are reported. Polymerization of ethylene and cyclopentene using a living bis(phenoxyimine)titanium catalyst yields copolymers with *cis*-1,2 cyclopentane units, high molecular weights, and low polydispersities. The effects of cyclopentene concentration, ethylene pressure, and reaction temperature on cyclopentene incorporation were determined; under the optimal reaction conditions 47 mol % cyclopentene was incorporated to give a nearly perfectly alternating copolymer. The glass-transition temperatures of the polymers, ranging from −27.3 °C (27 mol % cyclopentene) to 10.1 °C (47 mol % cyclopentene), were found to be linearly dependent on the mole percent cyclopentene content. Synthesis of atactic and isotactic model poly(ethylene-*alt*-(*cis*-1,2-cyclopentane))s using ring-opening metathesis polymerization allowed the assignment of the fine structure of ^{13}C NMR spectra of atactic polymers made from ethylene and cyclopentene. Finally, polymers containing blocks with varying ratios of ethylene/cyclopentene were synthesized. By repetitively raising and lowering the ethylene pressure of a cyclopentene/ethylene polymerization, polymers with multiple blocks were synthesized.

Introduction

The development of homogeneous polymerization catalysts over the past two decades has made possible the synthesis of a wide range of macromolecules of defined architecture. Catalysts are now available that offer unprecedented control of polymer stereochemistry, functionality, molecular weight, and composition.[1−4] One of the remaining challenges in polymerization catalysis, especially regarding olefin polymerization, is the synthesis of ordered copolymers that have either block or alternating sequences. Although recent advances in living olefin polymerization have provided new routes to block copolymers by the sequential addition of monomer,[5] there are relatively few methods for the synthesis of alternating polymers. For example, alternating olefin/CO polymers have been synthesized,[6−8] owing to the discovery of catalysts that cannot homopolymerize either monomer but have excellent rates for monomer cross-propagation (CO following olefin and vice versa). An alternate strategy for the synthesis of alternating polyolefins is the utilization of a catalyst where the rate of homopolymerization of one monomer is significantly greater than that of the other monomer. By increasing the concentration of the less readily polymerized monomer, a high degree of alternation is attained in some cases. Although this strategy often produces polymers that are not perfectly alternating, it is more general as few catalysts are capable of cross-propagation in absence of homopropagation. Ethylene is a commonly employed monomer in alternating copolymerizations, as many catalysts polymerize it at least an order of magnitude faster than other olefin monomers. Alternating polymerizations of ethylene with styrene,[9−14] isobutylene,[15] norbornene,[16−26] propylene,[27−30] and other α-olefins[31−34] have recently been reported.

Cycloolefin copolymers have potential uses as engineering plastics.[35−37] Kaminsky reported the homopolymerization of cyclopentene using an *ansa*-zirconocene catalyst with methylaluminoxane (MAO). The resulting polycyclopentene, originally assigned a structure resulting from *cis*-1,2 insertion,[38] was later found to be formed by 1,3-enchainment (insertion, elimination, rotation, and reinsertion produces 1,3-linkages).[39,40] Kaminsky has also used metallocenes to synthesize polynorbornene.[41] McLain and Brookhart produced polycyclopentene with *cis*-1,3-enchainment, prepared by diimine nickel and palladium catalysts.[42] One of the problems of poly(cyclic olefin)s is their high melting point (T_m) and glass transition temperature (T_g), which are close to the decomposition temperatures of the polymers.[35] Therefore, ethylene/cycloolefin copolymers have been studied in order to access lower T_g polymers, as their T_g decreases proportionally with increasing ethylene content.[43] The introduction of a comonomer also leads to improved processability of the polymers. Copolymers with higher ethylene content display a wide range of glass transition temperatures, from low to ambient temperatures. Therefore, these materials have promise as segments of elastomers. Cycloolefin copolymers have great potential for high-performance materials with thermal stability, good transparency, high refractive index, high stiffness or softness, chemical resistance, and good processability.[35] Kaminsky prepared copolymers of cyclopentene and ethylene with up to 37 mol % cyclopentene incorporation through 1,2- and 1,3-enchainment.[43] Müller reported the copolymerization of ethylene and cyclopentene with a metallocene catalyst as well as the assignment of the ^{13}C NMR spectrum of the copolymer.[44] Up to 64 mol % of the cyclopentene units are incorporated via 1,3-enchainment. Although a number of cyclopentene−ethylene copolymerizations using several metallocene catalysts were performed recently, these copolymers have a mixed microstructure of 1,2- and 1,3-enchained cyclopentene units together with ethylene−ethylene and cyclopentene−cyclopentene monomer sequences.[45]

In 1961, Natta reported alternating ethylene/2-butene copolymers using a vanadium catalyst.[46] Subsequently,

10.1021/ma021353g CCC: $22.00

he reported the copolymerization of cyclopentene with ethylene in the presence of vanadium precatalysts and alkylaluminum cocatalysts.[47] Fractionation of the crude polymer yielded an octane insoluble portion that was proposed to be an alternating cyclopentene–ethylene copolymer ($T_m \sim 184$ °C). Although the microstructure of this alternating copolymer was not reported, Natta suggested that this crystalline polymer was erythro-isotactic based upon X-ray analysis. Furthermore, Natta reported cyclopentene polymerization with $VCl_4/AlEt_3$, $VOCl_3/AlEt_3$, or $V(acac)_3/AlEt_3$ to give poly(cyclopentene-*alt*-ethylene). Small quantities of ethylene sufficient for copolymer formation are generated during the reaction, presumably resulting from $AlEt_3$ decomposition.[48]

Insertion of cyclopentene into the metal–carbon bond of a polymerization catalyst results in a secondary alkyl group that resists further reaction. As a result, elimination reactions begin to compete with propagation, resulting in isomerization and chain termination events. On the basis of the success of vanadium catalysts for ethylene/cyclopentene copolymerizations, we reasoned that a class of living phenoxyimine-ligated titanium catalysts, discovered independently by our group and researchers at Mitsui Chemicals, might be suitable catalysts for such polymerizations.[49–53] Fujita and coworkers have recently reported the application of a pyrrolide–imine ligated titanium catalyst for the copolymerization of ethylene and norbornene.[26] Herein, we report the synthesis of highly alternating ethylene–cyclopentene copolymers. Microstructural analysis using ^{13}C NMR is performed by comparing the polymers to perfect model compounds prepared using ring-opening metathesis polymerization (ROMP). Characterization of the polymers using differential scanning calorimetry is reported. Finally, using a sequential addition polymerization procedure, a new class of ethylene/cyclopentene block copolymers is synthesized.

Results and Discussion

Syntheses of Model Polymers. To analyze the sequence and tacticity of ethylene/cyclopentene copolymers, we decided to explore the use of ROMP to synthesize model polymers.[54] Grubbs and Wu have reported the metathesis polymerization of bicyclo[3.2.0]hept-6-ene using a ruthenium-based catalyst.[55] Hydrogenation of the polyolefin yields a saturated polymer which is a perfect model for an alternating ethylene/cyclopentene copolymer. Because of the structure of the monomer, the cyclopentene units of the polymer are connected to the main-chain with *cis*-1,2 stereochemistry. Using Grubbs' procedure (Figure 1),[56] we recently synthesized poly(bicyclo[3.2.0]hept-6-ene) with ruthenium carbene **1**. The ^{13}C NMR spectrum of the polymer shows that cis and trans olefins are present in the polymer main chain in a 2.7:1 ratio,[57] and the broadness of the peaks is indicative of the absence of tacticity.[58] Hydrogenation of the polymer using *p*-toluenesulfonhydrazide yields the alternating cyclopentene–ethylene model copolymer which was analyzed using ^{13}C NMR spectroscopy (Figure 2).[56] The peaks in the spectrum were assigned by estimating the shielding effects of the substituents of the polymer backbone;[59] these assignments of ring structure agreed with those proposed in the literature with the exception of the assignment of C_1 carbons.[44,45] Fine structure in the peaks of the NMR spectrum indicate the lack of tacticity of the polymer. The peak for the methine of the polymer (C_2) appears to exhibit triad resolution, the C_3 methylene exhibits dyad resolution, and C_1 appears to exhibit triad/tetrad resolution, while C_4 is insensitive to stereochemistry. The fine structures of the shifts for C_2 and C_3 have been tentatively assigned (Figure 2) on the basis of Bernoullian statistics ($P_m = 0.34$) in combination with the shifts for the purely isotactic polymer (vide infra). There is ambiguity in the assignment of the mr and rm triads of C_2 due to statistical equivalence. This polymer is slightly syndiotactic, with 66% racemic dyads in the main chain. The polymer is predominantly amorphous with a T_g of 19 °C and a melting transition peaking at 123 °C.[58]

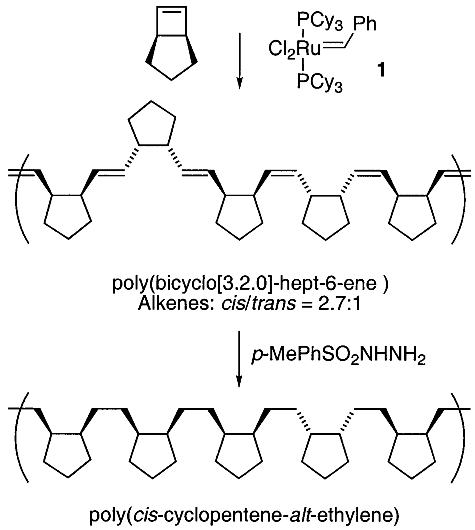

Figure 1. Synthesis of poly(*cis*-cyclopentene-*alt*-ethylene).

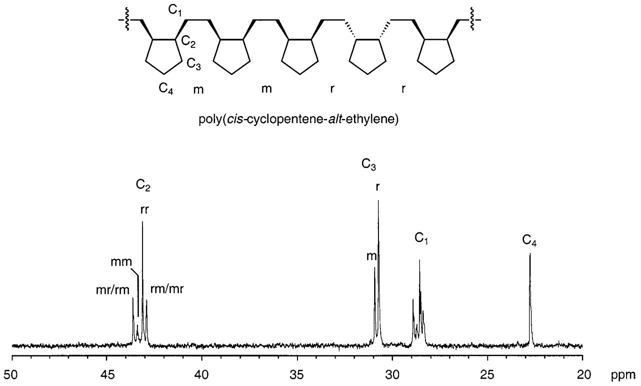

Figure 2. ^{13}C NMR spectrum (100 MHz) of perfectly alternating, slightly syndiotactic poly(cyclopentene-*alt*-ethylene). The polymer was made by hydrogenation of the ROMP polymer of bicyclo[3.2.0]hept-6-ene which was made using $Cl_2(PCy_3)_2Ru{=}CHCPh$ (**1**).

Schrock and co-workers have reported that chiral molybdenum carbene complexes can ROMP norbornadienes to yield highly isotactic polymers with *cis*-alkenes in the main chain.[60,61] We therefore decided to employ chiral complex *rac*-**2** for the polymerization of bicyclo[3.2.0]hept-6-ene (Figure 3).[62] The ^{13}C NMR spectrum of the polymer shows that only cis olefins are present in the polymer main chain,[57] and because of the sharpness of the four peaks present, the polymer appears to be highly tactic.[58] Highly cis-configured polynorbornadienes produced with chiral molybdenum complexes typically highly show isotactic microstructures.[60,61] Therefore, we tentatively assign the microstructure of this polymer to be isotactic. Hydrogenation of the polymer

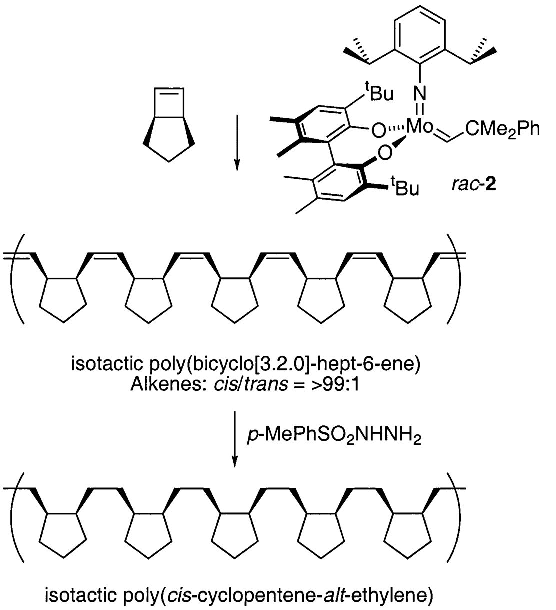

Figure 3. Synthesis of isotactic poly(*cis*-cyclopentene-*alt*-ethylene).

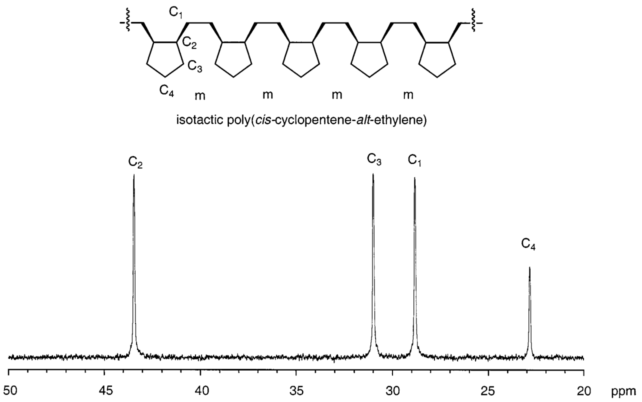

Figure 4. ^{13}C NMR spectrum (100 MHz) of perfectly alternating isotactic poly(*cis*-cyclopentene-*alt*-ethylene). The polymer was made by hydrogenation of the ROMP polymer of bicyclo[3.2.0]hept-6-ene, which was made using catalyst *rac*-**2**.

using *p*-toluenesulfonhydrazide yields the isotactic, alternating cyclopentene−ethylene copolymer. The polymer is semicrystalline with a T_g of 17 °C and melting transition peaking at 182 °C.[58] The lack of fine structure in the peaks of the ^{13}C NMR spectrum of the polymer indicates a high degree of tacticity (Figure 4). Notably, the spectrum exhibits peaks that match the major shifts of a partially alternating ethylene/cyclopentene polymer made using $V(acac)_3/Et_2AlCl$, which was proposed to be isotactic by Natta.[47,58]

Alternating Copolymerization of Ethylene and Cyclopentene. The catalyst system **3**/MAO[49] ([Al]/[Ti] = 150, [Ti] = 2.5 mM) was added to cyclopentene (7.1 M) in toluene at 70 °C. No polymer was formed over a period of 16 h. However, copolymerization of cyclopentene and ethylene was carried out using **3** with MAO under a variety of conditions to yield ethylene/cyclopentene copolymers (Figure 5, Table 1). The yield of polymer decreased with decreasing ethylene pressure, and below 1 psi of ethylene pressure, the activity was extremely low. These results are consistent with the observation that the reactivity of ethylene is much greater than that of cyclopentene. Molecular weight distributions of the cyclopentene/ethylene copolymers ($M_w/M_n = 1.17-1.41$) are much narrower than conventional polymers that were obtained by homogeneous catalysts such as metallocenes, consistent with living polymerizations. It should be noted that the number of chains formed, per molecule of **3**, is less than 1. The fraction of active chains, which can be estimated by the polymer yield, moles of catalyst, and M_n of the polymer, is less than 0.5 for the entries in Table 1.[63] Since this number depends on the M_n, which is determined by GPC and is thus relative to polystyrene, it is not possible to determine the precise number of active chains. However, it is clear that the fraction of active chains decreases with increased reaction temperature as well as decreasing ethylene pressure. Because of the narrow polydispersities of the polymers formed, we believe the decreases in percentage of active chains is due to conditions during the activation of **3**. Therefore, current work focuses on new methods for efficient activation.

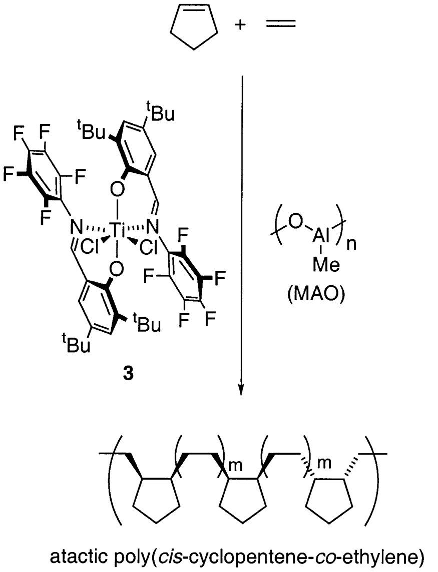

Figure 5. Copolymerization of ethylene and cyclopentene using **3**/MAO (polymer is alternating when *m* ∼ 1).

All of the polymers have isolated cyclopentene units, since the rate of cyclopentene homopolymerization is essentially zero. In addition, the cyclopentene units are incorporated solely via cis-1,2-enchainment between 0 and 25 °C as determined by ^{13}C NMR. Cyclopentene incorporation, again determined by ^{13}C NMR, decreases with increasing ethylene pressure as well as decreasing reaction temperature. When the polymerization was carried out at 40 °C with lower ethylene pressure (Table 1; entries 5 and 8), peaks derived from 1,3-enchainment of cyclopentene were observed (40.8, 40.5, 40.3, and 31.8 ppm).[44,45,58] The percentage of 1,3-enchainment of cyclopentene was only 1−6% compared to total cyclopentene units. It is known that cyclopentene−ethylene copolymers derived from metallocene catalysts show a significant amount of 1,3-enchainment of cyclopentene.[44,45] Using metallocene catalysts, the polymerization must be carried out with appreciable ethylene concentration in order to observe perfect 1,2-enchainment of cyclopentene units in the copolymers; under these conditions, cyclopentene incorporation is low.[45] In comparison with the methylene carbon region of ^{13}C NMR spectrum of the polymer synthesized using ruthenium catalyst **1** (Figure 2), the signals at 29.1−30.1 ppm are due to the ethylene−ethylene sequences for the alternating copolymer prepared from **3** (Figure 6; Table

Table 1. Ethylene/Cyclopentene Copolymerization Using 3/MAO[a]

entry	**3** (μmol)	ethylene (psi)	time (h)	cyclopentene (mmol)	T_p (°C)	productivity [kg/(mol Ti h)]	M_n[b] (g/mol × 10^{-3})	M_w/M_n[b]	cyclopentene content[c] (mol %)	1,3-units[c] (%)	T_g[d] (°C)
1	20[e]	10	1	50	0	49	103	1.17	27	0	−27.3
2	40	5	3	200	40	25	221	1.34	33	0	−14.7
3	20[e]	3	6	150	0	13	158	1.21	33	0	−13.3
4	20[e]	3	3	150	25	15	133	1.24	36	0	−4.5
5	20[e]	3	3	150	40	4	70	1.41	41	1	4.5
6	40	1	6	150	0	6	100	1.19	39	0	−3.2
7	40	1	6	150	25	4	169	1.30	40	0	0.5
8	40	1	7	150	40	0.8	121	1.31	44	6	3.4
9	60	<1	24	150	25	0.03	21	1.34	47	0	10.1

[a] General conditions: **3** in toluene (5 mL) added to a MAO solution ([Al]/[Ti] = 150), and then ethylene was added. [b] Determined by GPC in 1,2,4-trichlorobenzene at 140 °C vs polystyrene standards. [c] Determined by ^{13}C NMR. [d] Determined by DSC. [e] **3** disssolved in 3 mL of toluene.

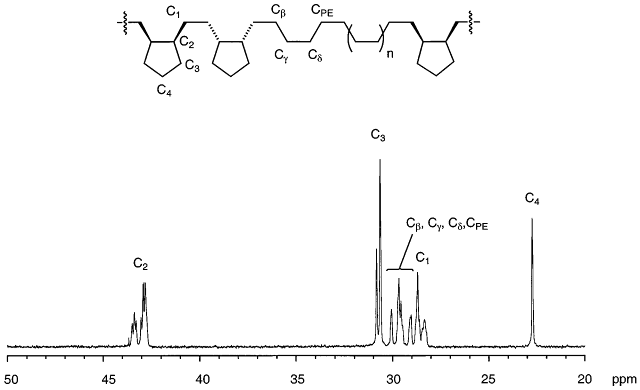

Figure 6. ^{13}C NMR spectrum (100 MHz) of the cyclopentene−ethylene copolymer synthesized by **3**/MAO (Table 1, entry 7).

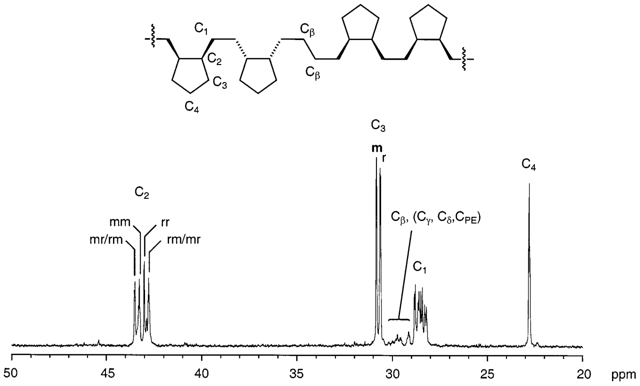

Figure 7. ^{13}C NMR spectrum (100 MHz) of the cyclopentene−ethylene copolymer synthesized by **3**/MAO (Table 1, entry 9).

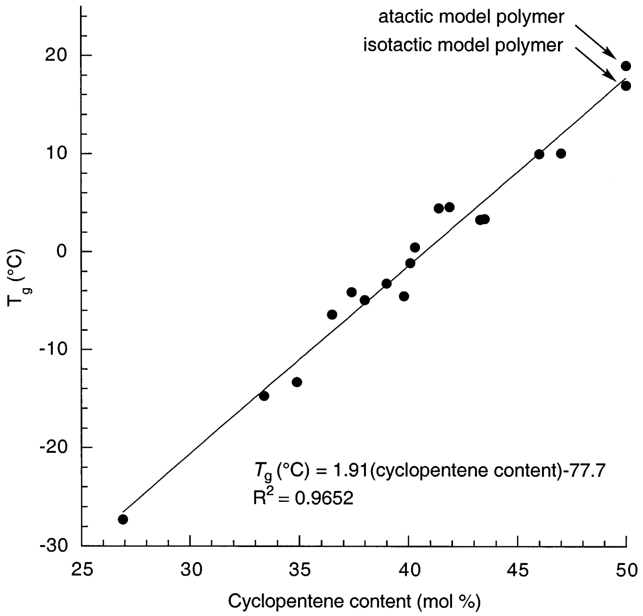

Figure 8. Glass transition temperature (T_g) vs cyclopentene content of cyclopentene/ethylene copolymers.

1, entry 7). The cyclopentene content increased up to 47 mol % by decreasing the ethylene pressure. When ethylene pressure was under 1 psi, almost perfectly alternating cyclopentene−ethylene copolymer was synthesized (Figure 7; Table 1, entry 9). On the basis of the microstructual assignments of these polymers (vide supra), the alternating copolymers made using **3**/MAO are completely atactic.

The correlation between T_g and cyclopentene content is shown in Figure 8. The T_g increases with increasing cyclopentene content. The equation relating T_g and cyclopentene content is T_g (°C) = 1.91 (mol % cyclopentene) − 77.7.

Block Copolymer Synthesis. Given the established living nature of olefin polymerization with phenoxyimine-based titanium catalysts[49−53] and the narrow polydispersities of the cyclopentene/ethylene copolymers, we decided to explore the synthesis of block copolymers with this catalytic system. When catalyst precursor **3** (2.7 mM) was added to a solution of MAO ([Al]/[Ti] = 150) in toluene (10 mL) at 0 °C in the presence of ethylene (40 psi), a living polyethylene (A-block) was formed after 2 min (M_n = 115 000 g/mol, M_w/M_n = 1.26). Subsequently, the ethylene pressure was lowered to 2 psi, and cyclopentene (20 mL) was added to the reactor. After 6 h of additional polymerization time, a higher molecular weight diblock polymer (AB diblock) was formed (M_n = 211 000 g/mol, M_w/M_n = 1.32) (Tables 2 and 3; entry 1). ^{13}C NMR spectroscopy was consistent with a polyethylene-*block*-poly(cyclopentene-*co*-ethylene) microstructure with a total cyclopentene content of 17 mol %. On the basis of this value and the number-average molecular weights of the A-block and AB-diblock, it can be estimated that the cyclopentene content of the B-block is 38%.[64] DSC analysis revealed glass transition temperatures at −27.3 and 1.6 °C, the average of which corresponds to a cyclopentene content of 34 mol % based on the equation derived using Figure 8. The presence of two T_g's is not understood at the current time, but it suggests two separate amorphous domains. DSC analysis also revealed a peak melting temperature of 125.6 °C, expected for a phase-separated polyethylene domain.

In addition, we were also interested in making triblock copolymer systems, as these materials can have enhanced mechanical properties relative to the related diblock copolymers. As described previously, the cyclo-

Table 2. Synthesis of Block Copolymer of Ethylene (A) and Ethylene/Cyclopentene ((B) and (C)) Using 3/MAO

		A-block		B-block			C-block			
entry	T_p (°C)	ethylene (psi)	time (min)	ethylene (psi)	cyclopentene (mmol)	time (h)	ethylene (psi)	cyclopentene (mmol)	time (min)	polymer yield (g)
1	0[a]	40	2	2	230	6	NA	NA	NA	2.71
2	0[b]	15	3	3	115	1	60	115	3	0.68
3	25[c]	30	2	3	150	0.5	30	150	2	1.27

[a] Conditions: **3** (40 μmol) in toluene (5 mL) added to a MAO solution (10 mL of toluene, [Al]/[Ti] = 150). Ethylene was added to synthesize the A-block. The B-block (poly(cyclopentene-*co*-ethylene)) was grown from the A-block by adding cyclopentene (230 mmol) to the polymerization. [b] Conditions: **3** (20 μmol) in toluene (5 mL) added to a MAO solution (10 mL of toluene, [Al]/[Ti] = 150). After AB-diblock synthesis, the C-block (poly(cyclopentene-*co*-ethylene)) was grown from the AB-diblock by increasing the ethylene pressure. [c] Conditions: **3** (10 μmol) in toluene (5 mL) added to a MAO solution (40 mL of toluene, [Al]/[Ti] = 150). After the ABC-triblock synthesis, the conditions for B- and C-block synthesis were repeated five times to produce a $A(BC)_6$ multiblock polymer.

Table 3. Characterization of Block Copolymers Produced Using Conditions in Table 2

		A-block		total						
entry	no. of block segments	M_n (g/mol × 10^{-3})[a]	M_w/M_n[a]	M_n (g/mol × 10^{-3})[a]	M_w/M_n[a]	cyclopentene content (mol %)[b]	T_{g1} (°C)[c]	T_{g2} (°C)[c]	T_{m1} (°C)[c]	T_{m2} (°C)[c]
1	2	115	1.26	211	1.32	17.4	−27.3	1.6	125.6	
2	3[d]	32	1.27	138	1.20	15.3	−28.3	−3.2	119.6	90.0
3	13	ND[e]	ND[e]	2741	1.38	4.5	−17.2		116.4	104.6

[a] Determined by GPC in 1,2,4-trichlorobenzene at 140 °C vs polystyrene standards. [b] Determined by ^{13}C NMR. [c] Determined by DSC. [d] AB-diblock; M_n = 109 000 g/mol, M_w/M_n = 1.22. [e] ND = not determined.

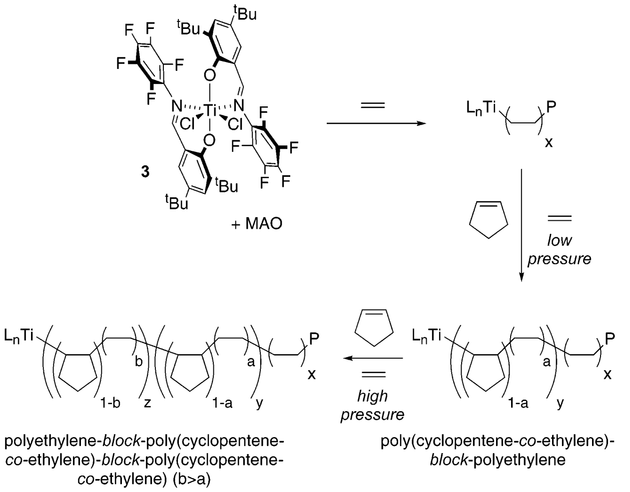

Figure 9. Synthesis of block copolymers of ethylene and cyclopentene using **3**/MAO.

pentene/ethylene copolymer composition can be controlled by varying the ethylene feed, as higher ethylene pressures giving correspondingly higher ethylene content in the copolymer. We realized that this feature could be used to synthesize block copolymers with blocks of differing ethylene content by simply changing the ethylene pressure during the course of the polymerization. While high ethylene pressures rapidly generate a crystalline ethylene-rich copolymer, lower pressures permit more cyclopentene insertion and give an amorphous copolymer with higher cyclopentene content. According to this strategy, a triblock copolymer was synthesized using a sequential addition variable pressure approach (Figure 9, Tables 2 and 3; entry 2). As described previously, catalyst **3** (1.3 mM) was added to a solution of MAO ([Al]/[Ti] = 150) in toluene (10 mL) at 0 °C in the presence of ethylene (15 psi), giving a monodisperse polyethylene (A-block) after 3 min (M_n = 32 000 g/mol, M_w/M_n = 1.27). Addition of cyclopentene (10 mL) while reducing the ethylene pressure to 3 psi for 1 h produced a polyethylene-*block*-poly(cyclopentene-*co*-ethylene) diblock (AB-diblock) copolymer (M_n = 109 000 g/mol, M_w/M_n = 1.22; T_m = 120.6 °C, T_g = −28.5 and −2.4 °C). Finally, the ethylene pressure was returned to 60 psi for 3 min, giving a copolymer with M_n = 138 000 g/mol and M_w/M_n = 1.20. The shift of GPC traces after each step in the synthesis of the ABC triblock copolymer strongly suggests that this process is proceeds in a living fashion (Figure 10). The resulting polymer is an ABC-triblock composed of one pure polyethylene domain and two poly(cyclopentene-*co*-ethylene) segments of high (B-block) and low (C-block) cyclopentene content, respectively. At the current time, we are unable to tell the precise composition and distribution of cyclopentene in blocks B and C. DSC analysis of the final triblock copolymer revealed melting transitions of the two semicrystalline domains (Figure 11b). The T_m of 119.6 °C is consistent with polyethylene (A-block), while the lower T_m of 90.0 °C is presumably derived from the ethylene-rich copolymer domain (C-block). The two T_g's at −28.3 and −3.2 °C are close to those for the AB-diblock copolymer (Figure 11a) and are due to the ethylene-*co*-cyclopentene B-block.

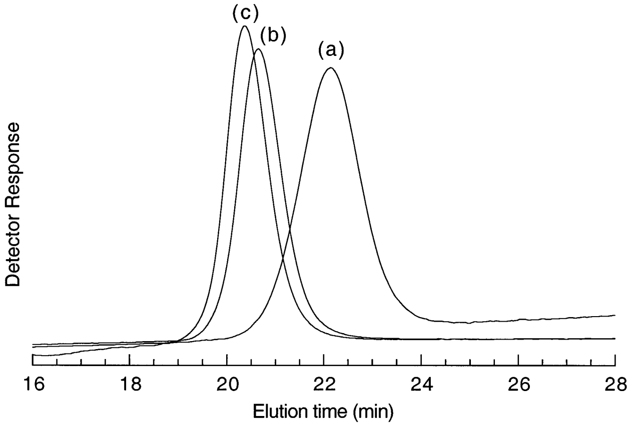

Figure 10. GPC traces of the ABC-triblock copolymer after each step in the polymerization: (a) polyethylene (A-block, M_n = 32 000, M_w/M_n = 1.27), (b) polyethylene-*block*-poly(cyclopentene-*co*-ethylene) (AB diblock, M_n = 109 000, M_w/M_n = 1.22), (c) polyethylene-*block*-poly(cyclopentene-*co*-ethylene)-*block*-poly(cyclopentene-*co*-ethylene) (ABC triblock, M_n = 138 000, M_w/M_n = 1.20).

Furthermore, the synthesis of a multiblock copolymer was attempted using the same procedure. On the basis of the sequence of monomer addition, this material

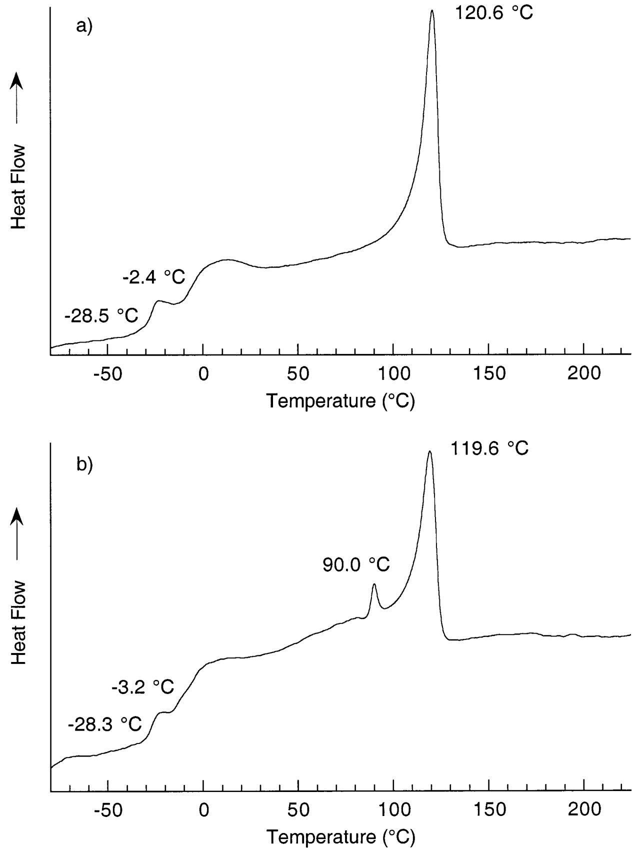

Figure 11. DSC profile of the block copolymers synthesized by using **3**/MAO (Table 3, entry 2). (a) DSC profile of the AB-diblock copolymer. (b) DSC profile of the ABC-triblock copolymer.

should be composed of one pure polyethylene domain and 12 sequential poly(cyclopentene-*co*-ethylene) segments of high (B-block) and low (C-block) cyclopentene content, respectively. The T_m of 116.4 °C is consistent with polyethylene (A-block), while the slightly lower T_m of 104.6 °C is presumably derived from the copolymer domain of higher ethylene content (C-block). An average T_g of −17.2 °C, derived from the amorphous segment, is consistent with a cyclopentene content of 32 mol % using the correlation derived from the related copolymers (Figure 8).

Conclusion

Polymerization of ethylene and cyclopentene using a living fluorinated bis(phenoxyimine)titanium catalyst yields copolymers with isolated, *cis*-1,2-cyclopentane units, high molecular weights, and low polydispersities. Under the optimal reaction conditions (very low ethylene pressure at 25 °C), cyclopentene was incorporated to give a nearly perfectly alternating copolymer (cyclopentene content 47 mol %). The glass-transition temperatures of the polymers, ranging from −27.3 °C (27 mol % cyclopentene) to 10.1 °C (47 mol % cyclopentene), were revealed to be linearly dependent on mole percent cyclopentene content.

Furthermore, atactic and isotactic model poly(ethylene-*alt*-(*cis*-1,2-cyclopentane))s were prepared by ring-opening metathesis polymerization and subsequent hydrogenation. These polymers allowed the assignment of the fine structure of ^{13}C NMR spectra of atactic polymers made from ethylene and cyclopentene using bis(phenoxyimine)titanium catalyst. Finally, polymers containing blocks with varying ratios of ethylene/cyclopentene were synthesized by repetitively raising and lowering the ethylene pressure of a cyclopentene/ethylene polymerization. Changing the ethylene pressure during the reaction gives several kinds of block copolymers, ranging from AB diblock to A(BC)$_n$ multiblock polymers.

Experimental Section

General Considerations. All reactions with air- and/or water-sensitive compounds were carried out under dry nitrogen using a MBraun Labmaster drybox or standard Schlenk line techniques. ^{13}C NMR spectra of the polymers (dissolved in 1,1,2,2-tetrachloroethane-d_2) were obtained at 95 or 120 °C on a Varian VXR-400 spectrometer at 100 MHz. The spectra were referenced vs residual nondeuterated solvent shifts, $\delta = 74.0$ ppm. An inverse gated decoupling sequence was employed with a 30° pulse width over a 160 ppm spectral width at a 2.0 s acquisition time to minimize NOE and allow for quantitative analysis. Enough scans were accumulated to ensure a sufficient signal-to-noise ratio. Molecular weights (M_w and M_n) and polydispersities (M_w/M_n) were determined by high-temperature gel permeation chromatography (GPC). All analyses were performed with a Waters Alliance 2000 liquid chromatograph equipped with a Waters DRI detector and a Jordi styrene−divinylbenzene linear mixed-bed column. The GPC columns were eluted with 1,2,4-trichlorobenzene (TCB) containing 0.1 wt % Irganox 1010 at 140 °C at 1.0 mL/min and were calibrated using 23 monodisperse polystyrene standards. Polymer samples were typically placed in a 140 °C oven for 24 h to eliminate supermolecular aggregates prior to molecular weight measurements. DSC analyses were performed on a Seiko DSC 220C instrument using EXSTAR 6000 processing software. The measurements were made in aluminum crimped pans under nitrogen with a heating rate 10 °C/min from −100 to 300 °C. The reported values originate from the second heating scan.

Materials. Diethyl ether, hexane, and toluene were distilled from sodium benzophenone ketyl under nitrogen. 1,3-Cycloheptadiene was purchased from Aldrich and used as received; bicyclo[3.2.0]hept-6-ene was prepared as described earlier.[65,66] V(acac)$_3$ and Et$_2$AlCl were purchased from Aldrich. The ruthenium complex Cl$_2$(PCy$_3$)$_2$Ru=CHPh (**1**) and 2,6-diisopropylphenylimidoneophylidene[*rac*-BIPHEN]molybdenum(VI) (**2**) were purchased from Strem. Methylaluminoxane (PMAO-IP, 12.6 wt % Al in toluene) was purchased from Akzo Nobel. Cyclopentene was purchased from Aldrich. Cyclopentene was dried over calcium hydride for 12−16 h at room temperature and then distilled. Titanium complex **3** was prepared as described earlier.[49]

Cyclopentene Homopolymerization Using 3/MAO. Polymerizations were conducted in a 3 oz Lab-Crest pressure reaction vessel equipped with a magnetic stir bar. The reactor was first conditioned under dynamic vacuum and high temperature and then charged with a 3 mmol of PMAO and 5 mL of cyclopentene under nitrogen. The 20 μmol of **3** was dissolved in toluene (3 mL) at room temperature under nitrogen. The solution was then added to the reactor using a syringe. Finally, the reactor was adjusted at 70 °C. After 16 h, the reactor was vented, and the solution was poured to the methanol/HCl. No polymer was obtained.

Cyclopentene/Ethylene Copolymerization Using 3/MAO. Polymerizations were conducted in a 3 oz Lab-Crest pressure reaction vessel equipped with a magnetic stir bar. In a typical polymerization experiment, the reactor was charged with 6 mmol of PMAO under nitrogen. Then 13.2 mL of cyclopentene was introduced. **3** was dissolved in toluene (5 mL) at room temperature under nitrogen. The solution was then added to the reactor via syringe, such that the fixed Al/Ti ratio was 150. Finally, the reactor was pressurized with ethylene gas and adjusted to the desired pressure and temperature. After the desired period of time, the reactor was vented. The polymer was precipitated from methanol/HCl, filtered, and then dried in vacuo to constant weight.

Poly(cyclopentene-*co*-ethylene) Synthesized from 3/MAO. ^{13}C NMR (100 MHz, $C_2D_2Cl_4$): δ 43.5, 43.4, 43.3, 43.0, 42.9, 42.8 (C_2), 30.9, 30.7 (C_3), 30.1, 29.7, 29.6, 29.1 (C_β, C_γ, C_δ, C_{PE}), 28.8, 28.7, 28.6, 28.5, 28.4, 28.3 (C_1), 22.8 (C_4).

Synthesis of Polyethylene-*block*-poly(cyclopentene-*co*-ethylene) and Polyethylene-*block*-poly(cyclopentene-*co*-ethylene)-*block*-polyethylene. Polymerizations were conducted in a 6 oz Lab-Crest pressure reaction vessel equipped with a magnetic stir bar. The reactor was first conditioned under dynamic vacuum and high temperature and then charged with a desired amount of toluene and PMAO. The reactor was pressurized with ethylene gas and was adjusted to the desired pressure. Catalyst **3** was dissolved in toluene (5 mL) at room temperature under nitrogen and was syringed into the reaction after briefly lowering the ethylene pressure. The Al/Ti ratio was 150. After repressurizing with ethylene and stirring for the desired period of time, the reactor was vented, and cyclopentene was added by syringe. Then (1) the reactor was pressurized again with ethylene gas and was adjusted to the desired pressure. (2) After the desired period of time, ethylene pressure was increased up to desired pressure during the desired period of time, and then the reactor was vented. In the case of diblock polymerization, the operation of (2) was not carried out. In the case of triblock polymerization, the operations of (1) and (2) were carried out. After each step, a 1−2 mL aliquot was taken for GPC analysis. When multiblock copolymer was synthesized, the operations of (1) and (2) were repeated six times. After the desired period of time, the reactor was vented. The polymer was precipitated from methanol/HCl, filtered, and then dried in vacuo to constant weight.

Acknowledgment. G.W.C. gratefully acknowledges a Packard Foundation Fellowship in Science and Engineering, an Arnold and Mabel Beckman Foundation Young Investigator Award, a Camille Dreyfus Teacher-Scholar Award, a Sloan Fellowship, and an NSF CAREER Award. This work made use of the Cornell Center for Materials Research Shared Experimental Facilities, supported through the National Science Foundation Materials Research Science and Engineering Centers program (DMR-0079992). M.F. was supported by the Sumitomo Chemical Company, Limited.

Supporting Information Available: Additional synthetic procedures and polymer characterization (NMR and DSC). This material is available free of charge via the Internet at http://pubs.acs.org.

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MA021353G