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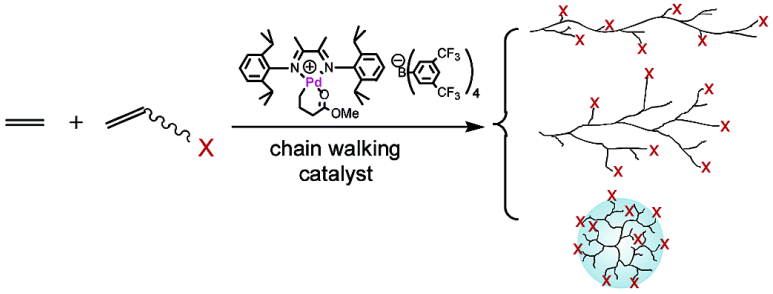

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Synthesis of Functional Olefin Copolymers with Controllable Topologies Using a Chain-Walking Catalyst

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Abstract: The branching topology of ethylene polar copolymers was for the first time successfully controlled by copolymerization of ethylene with polar olefins using a palladium-bisimine chain-walking catalyst, in which ethylene pressure and comonomer concentration were used to control the competition between isomerization (chain-walking) and monomer insertion processes. Although the overall branching density changes very slightly, the topology of the copolymers becomes more dendritic as the ethylene pressure and comonomer feed concentration are decreasing. This provides a straightforward one-pot synthesis to access a full range of functional copolymers having controllable branching topologies. To demonstrate the utility of this methodology, dendritic functional copolymers having hydroxyl, epoxide, and carbohydrate groups were prepared in a one-pot polymerization as potential functional materials.

Introduction

A tremendous amount of effort has been devoted to the design of new polymer architectures and topologies because of their importance to polymer properties.[1] We have been exploring a new strategy for controlling polymer branching topology through transition-metal catalysis.[2] Instead of designing new monomers and relying on stepwise synthesis, we were attempting to achieve new polymer topologies by controlling the covalent linkage of simple monomers through transition-metal-catalyzed polymerization. We have demonstrated this concept for two systems: (a) the free radical polymerization of divinyl monomers controlled by a cobalt-dioxime chain transfer catalyst,[2b] and (b) the coordination polymerization of ethylene[2a,c,e] using the Brookhart's palladium-bisimine olefin polymerization catalysts.[3] In the first system, hyperbranched polymers were obtained in a one-pot polymerization of simple commercial monomers by controlling the kinetic competition between radical chain propagation and chain transfer.[2b] In the second system, polyethylene (PE) branching topology was controlled by ethylene pressure (P_E) in ethylene polymerization using the chain-walking catalyst. By controlling the competition between monomer insertion and catalyst isomerization (chain-walking),[2a,3b,4] we synthesized PEs with a broad spectrum of topologies, ranging from linear to hyperbranched to dendritic.[2a,c,e] The PE physical properties change dramatically as the branching topology changes: from plastic to rubbery and eventually to a viscous liquid as the branching topology changes from linear to hyperbranched to dendritic. Concurrent with our studies, others have reported different systems using transition metal catalysts that polymerize ethylene to give branched to hyperbranched architectures.[5] Bazan and co-workers have reported the synthesis of polyolefins having controlled short-chain branches via a tandem action of multiple homogeneous catalysts − some for olefin oligomerization and the others for polymerization.[5a,b] Sen and co-workers have reported the synthesis of hyperbranched PEs having relatively low molecular weights using different nickel or palladium catalysts.[5c,d] *Our previous studies have demonstrated that high molecular weight PEs with a full range of branching topologies could be prepared in a one-pot polymerization using a single catalyst*.[2a,c,e] To broaden the scope of our strategy, we report here the control of the branching topology of ethylene polar copolymers through copolymerization using the chain-walking catalyst (Scheme 1).

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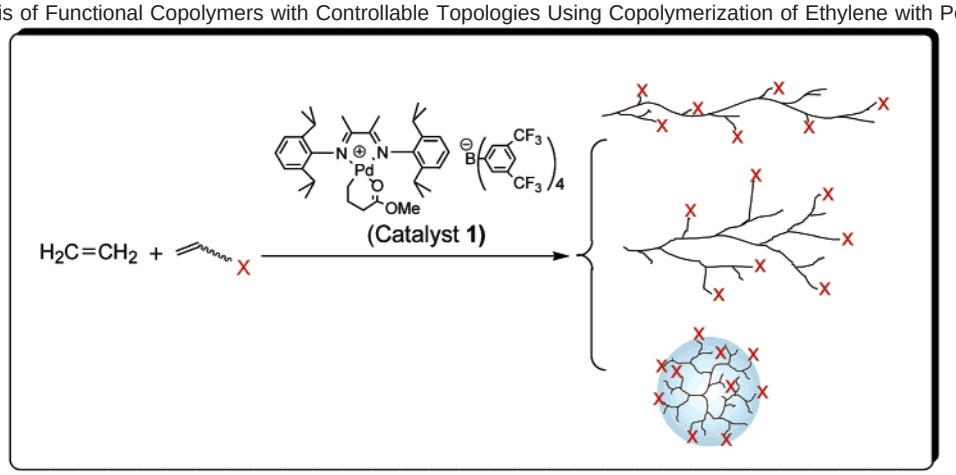
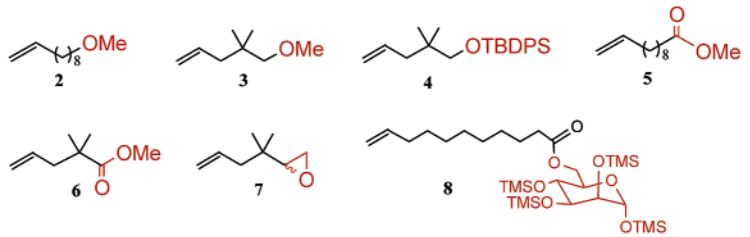
Scheme 1. Synthesis of Functional Copolymers with Controllable Topologies Using Copolymerization of Ethylene with Polar Comonomers



Polar comonomers:



Functional olefin copolymers are valuable materials because the functional groups contribute special properties to olefin polymers. Conventionally, they are produced by free radical copolymerizations of ethylene and polar comonomers at extremely high temperatures and high pressures.[6] Significant progress has been made in recent years in developing late transition-metal catalysts that can copolymerize olefins with polar comonomers at milder conditions.[3,7] Notable examples include the Pd-bisimine catalyst system reported by Brookhart and co-workers[3] and the neutral nickel catalyst reported by Grubbs and co-workers,[7] which can copolymerize ethylene with methyl acrylate, polar norbornene monomers, and other functional monomers. Most of the reported polar olefin copolymers, however, have simple linear topology. Given the importance of functional olefin copolymers and the dependence of polymer properties upon topology,[1] it is of both fundamental and practical interests to explore methods to control the branching topology of polar olefin copolymers.

In this paper, we wish to report our studies on controlling the branching topology of copolymers of ethylene with polar comonomers. In this study, we first chose ether and ester comonomers (**4**−**6**) as the model system to demonstrate that both the comonomer incorporation level and the branching topology of ethylene copolymers can be systematically controlled by varying the polymerization conditions. As an application of the methodology, we then applied this strategy to the synthesis of interesting dendritic copolymers containing hydroxyl, epoxide, and saccharide functionalities as potential functional materials.

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Results and Discussion

Copolymerization of Ethylene with Polar Comonomers. We chose polar comonomers containing protected hydroxyl, ester, epoxide, and saccharide groups to conduct the copolymerization studies. These functionalities were chosen because they are common and can be easily converted to other functional groups by postpolymerization treatments. The comonomers shown in Scheme 1 were copolymerized with ethylene at various conditions with the goal of controlling the polymer topology by polymerization conditions (Table 1). Initial copolymerization of ethylene with polar comonomers having free hydroxyl group yielded no polymers, indicating that the catalyst cannot tolerate the protic hydroxyl functionality. After hydroxyl was protected as a methyl ether, copolymerization of **2** with ethylene afforded no polymer either (entry 3), which is presumably due to chain-walking of the Pd catalyst to the β-carbon of the ether group followed by β-OMe elimination to deactivate the catalyst. It has been reported that ether groups undergo a facial elimination reaction if it is in the β-position of a transition metal.[8] To circumvent this problem, a quaternary carbon was introduced between the double bond and the ether group to block the Pd catalyst from walking to the β-carbon of the functional group. Ether comonomers **3** and **4** were successfully copolymerized with ethylene using catalyst **1** (Scheme 1 and Table 1). Copolymerization of ethylene with comonomer **3** yielded copolymers with significantly lower productivity and lower molecular weight than ethylene homopolymerization under comparable conditions (compare entries 4 and 2), which was presumably caused by chelation of the ether oxygen to the active Pd center. By protecting the oxygen with a bulky *tert*-butyldiphenylsilyl (TBDPS) group, we copolymerized comonomer **4** with ethylene to afford polymers with productivity and molecular weight

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Table 1. Summary of the Copolymerization Conditions, Results, and the Characterization Data for the Copolymers

	reaction conditions[a]			results				polymer properties			
					TON/h[c]						
entry	comonomer	conc. (C_M)	P_E (atm)	yield[b] (g)	C_2H_4	comonomer	comonomer incorp.[d]	$M_n^e \times 10^{-3}$	$M_w^e \times 10^{-3}$	R_g^e (nm)	branches /1000 CH_2[f]
1	none	N/A	1.0	2.0	892.8	N/A	N/A	283	395	18.2	100
2	none	N/A	0.1	1.6	179.1	N/A	N/A	200	317	9.0	103
3	**2**	(0.02 M)	0.1	0	N/A	N/A	N/A	N/A	N/A	N/A	N/A
4	**3**	(0.02 M)	0.1	0.4	26.8	0.4	0.9%	38	58	4.8	98 (98.9)
5	**4**	(0.30 M)	1.0	14.0	797.5	7.2	0.9%	342	820	33.8	99 (99.9)
6	**4**	(0.09 M)	0.3	12.7	257.3	2.4	0.9%	357	645	24.6	103 (103.9)
7	**4**	(0.03 M)	0.1	6.5	130.6	1.2	0.9%	300	483	15.6	105 (105.9)
8	**4**	(0.18 M)	0.1	3.5	73.8	3.8	4.9%	302	499	15.6	96 (100.9)
9	**4**[g]						4.9%	221	366	14.3	96 (100.9)
10	**4**	(0.36 M)	0.1	1.8	54.1	5.4	9.1%	370	727	18.2	89 (98.1)
11	**4**[g]						9.1%	169	355	17.5	89 (98.1)
12	**5**	(0.20 M)	0.1	0.5	21.3	1.9	8.2%	31	41	N/A[h]	105 (113.2)
13	**5**	(0.10 M)	0.1	0.9	23.3	1.2	4.9%	40	54	N/A[h]	106 (110.9)
14	**5**	(0.02 M)	0.1	1.7	38.9	0.4	0.9%	51	84	5.5	101 (101.9)
15	**6**	(0.90 M)	1.0	2.0	94.8	4.6	4.6%	77	114	12.2	97 (101.6)
16	**6**	(0.40 M)	0.3	1.6	60.0	2.7	4.3%	66	99	8.0	99 (103.3)
17	**6**	(0.09 M)	0.1	1.1	18.8	0.9	4.2%	45	85	6.0	101 (105.2)
18	**7**	(0.05 M)	0.1	1.5	117.6	2.5	2.1%	75	125	7.7	97 (99.1)
19	**8**	(0.02 M)	0.1	1.3	9.5	0.1	0.9%	71	87	6.2	99 (99.9)
20	**8**[g]						0.9%	63	80	5.4	99 (99.9)

[a] Catalyst load 2 mmol/L; solvents, chlorobenzene/toluene (1:3); reaction temperature, room temperature; reaction time, 16−48 h. [b] Yields based on isolated polymer mass. [c] TO/h is the catalyst turnover per hour. [d] mol %, data obtained from ^{1}H NMR. [e] Data obtained from SEC-MALS. [f] Data obtained from ^{1}H NMR. Data in parentheses are corrected branches/1000 CH_2 in which the branches ending with functional groups are added to the total branches. [g] Polymer obtained after the deprotection of TBDPS or TMS from the polymer shown in the previous entry. [h] Size too small to be measured accurately by MALS.

comparable to those of ethylene homopolymerization (comparing entries 1 and 2 with 5 and 8).

Copolymerization of **4** with ethylene was run at various ethylene pressures (P_E) and comonomer concentrations (C_M) (entries 5−11). As P_E and C_M decrease, the turnover rates (TON/h) for both ethylene and the comonomer decrease. The total branching density expressed as branches/1000 CH_2 remain relatively constant. The copolymerization was then run at constant P_E by varying C_M of **4** (entries 7, 8, and 10). As the C_M increases, the molar incorporation of the comonomer increases consistently, which agrees with previous reports of ethylene copolymerization with methyl acrylate.[3c] The apparent decrease of the total branching number with the increase of comonomer incorporation has to be corrected because the branches ending with functional comonomers were not counted in the calculation of the branching number. By adding the branches ending with functional comonomers, we found that the overall branching number remains relatively constant for a comonomer incorporation level up to 9.1 mol %.

A series of ester-containing comonomers were then copolymerized with ethylene at various conditions (entries 12−17). Brookhart and others have reported the ethylene/methyl acrylate (EMA) copolymerization using the Pd catalyst.[3] For the polymerization conditions employed in this study, however, the EMA copolymers have too low molecular weights to allow for the determination of their branching topology using multiangle light-scattering (MALS) measurements. As was discussed in the literature, the low molecular weight was caused by chelation of the ester group to the active Pd center during copolymerization.[3c] Using a comonomer having a longer spacer (comonomer **5**) or having a blocking quaternary carbon (comonomer **6**) led to significant improvement of both the productivity and the molecular weight. Presumably, the longer spacer or the steric repulsion between the quaternary carbon and the catalytic center reduce the tendency for chelation of ester group to the active Pd center. Following the same study as described for comonomer **4**, comonomer **5** was copolymerized with ethylene at constant P_E by varying the comonomer feed concentration. Again, the comonomer incorporation ratio increases consistently as C_M is increased. The comonomer **6** was employed in our further investigation of copolymer branching topology because the molecular weights of the copolymers of **6** were higher than those of **5**, hence facilitating the multi-angle light-scattering (MALS) studies.

Control of Copolymer Topology by Polymerization Conditions. Comonomers **4** and **6** were investigated in detail for the dependence of copolymer branching topology on copolymerization conditions. Our previous studies demonstrated that in ethylene homopolymerization the PE branching topology could be simply controlled by P_E, with linear PE being formed at high pressure and dendritic PE being obtained at very low pressure.[2a,c,e] Following the same strategy, **4** and **6** were copolymerized with ethylene at three pressures, 0.1, 0.3, and 1.0 atm, respectively. The comonomer C_M was adjusted proportionally to maintain a relatively constant comonomer incorporation ratio in the copolymers for comparison. The copolymerization data were summarized in Table 1 (entries 5−11 for **4** and 15−17 for **6**).

Following our previous studies,[2a,c,e] size exclusion chromatography (SEC) equipped with a refractive index and a MALS detector was used to measure the weight-averaged molecular weight (M_w) and the molecular size (R_g) of eluting fractions of polymer with the well-established expressions for classical light scattering:

$$\lim_{c\to 0} Kc/R_\Theta = \frac{1}{M_W}\{1 + 16\pi^2 n^2 R_g^2 \sin^2(\Theta/2)/3\lambda^2\} \quad (1)$$

where R_Θ is the Rayleigh ratio at scattering angle Θ, c is the concentration of the polymer, and K is equal to $4\pi^2 n^2 (dn/dc)^2/\lambda^4 N_A$, where n is the refractive index of the solvent, λ is the

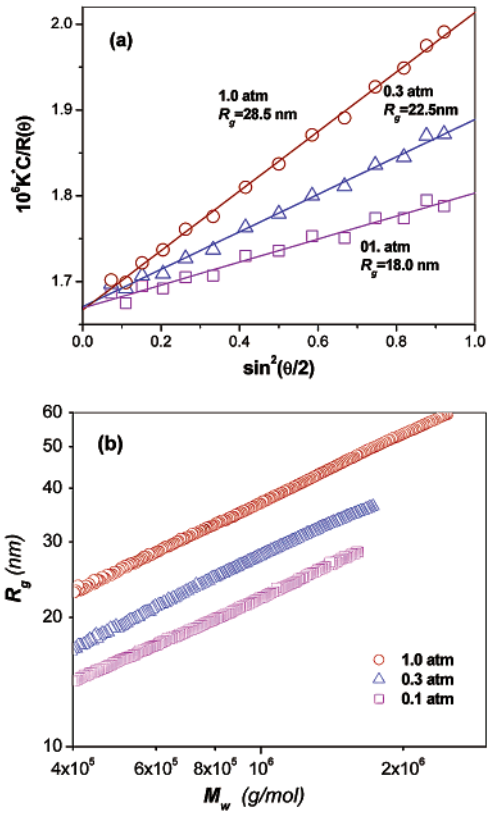


Figure 1. (a) Comparison of Debye plots for the fraction of copolymer at an M_w of 600 000 g/mol for the three ethylene copolymers of comonomer **4** made at 1.0 (○), 0.3 (△), and 0.1 (□) atm. (b) Correlation of R_g with M_w for the same three copolymers (entries 5−7 in Table 1).

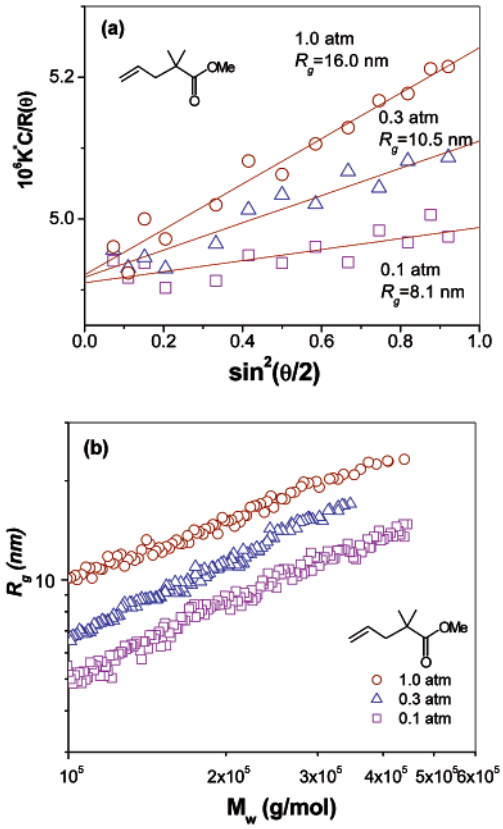


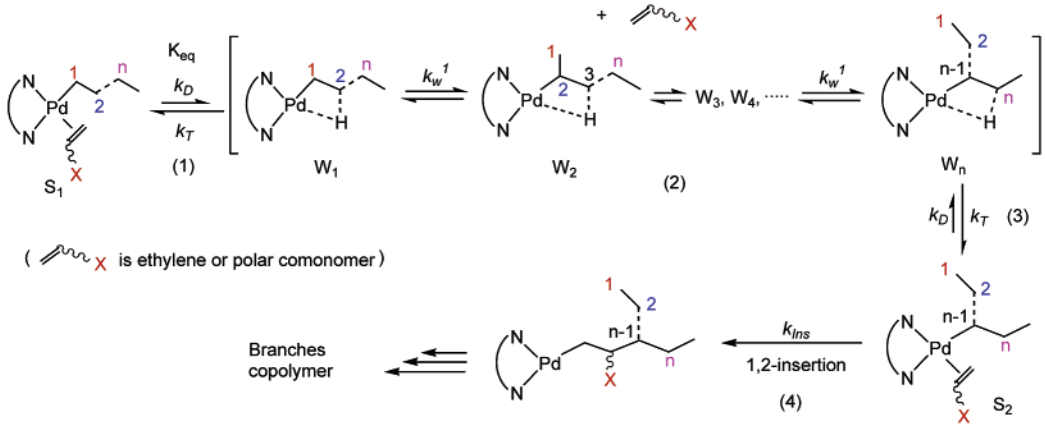
Figure 2. (a) Comparison of Debye plots for the fraction of copolymer at an M_w of 200 000 g/mol for the three ethylene copolymers of comonomer **6** made at 1.0 (○), 0.3 (△), and 0.1 (□) atm. (b) Correlation of R_g with M_w for the same three copolymers (entries 15−17 in Table 1).

wavelength of light, N_A is Avogadro's number, and d*n*/d*c* is the refractive index increment. The data for the copolymerization with comonomer **4** are discussed first. We observed that the R_g for the copolymers of **4** with similar M_w's increased with increasing P_E and C_M (entries 5−7). Because the online MALS detector measures M_w and R_g for every fraction of polymers eluted from the SEC column, we can compare the R_g at the same M_w for different samples. In Figure 1a, we compare the angular dependence of the fraction of copolymer of **4** at an M_w of 600 000 for the three samples that were made at 0.1, 0.3, and 1.0 atm, respectively. A large difference in the slope was observed, indicating that at the same M_w the R_g's are different. The R_g at $M_w = 600\,000$ was 18.0, 22.5, and 28.5 nm for the samples polymerized at 0.1, 0.3, and 1.0 atm, respectively. The separation of the polymer by SEC provides R_g as a function of M_w, and, as shown in Figure 1b, R_g consistently shifts upward as P_E and C_M were increased.

The same analysis was conducted for the copolymers with ester comonomer **6** (entries 15−17). Presumably, the ester group can still chelate to the active catalyst center during polymerization, and the molecular weights for the copolymers of **6** are significantly lower than those for the copolymers of **4**. Because the sizes of the copolymers of **6** are approaching the low detection limit of the MALS detector, the MALS data appear to be a little scattered as compared to the data for copolymers of **4**. Nevertheless, the same trend was observed as was seen for the copolymers of **4**. In Figure 2a, we compare the Debye plot for the fraction of copolymer of **6** at an M_w of 200 000 for the three samples that were made at 0.1, 0.3, and 1.0 atm, respectively. A large difference in the slope was observed, indicating that at the same M_w the R_g's are different. The R_g at $M_w = 200\,000$ was 8.1, 10.5, and 16.0 nm for the samples polymerized at 0.1, 0.3, and 1.0 atm, respectively. The correlation between R_g as a function of M_w shows again that R_g consistently shifts upward as P_E and C_M were increased (Figure 2b).

^{1}H NMR data (entries 5−7 for copolymers of **4** and 15−17 for copolymers of **6**), however, indicate that both the comonomer incorporation ratio and the total branching density are nearly constant for the copolymers made at different P_E and C_M. On the basis of our previous studies on ethylene homopolymerization,[2a,c,e] the change of the R_g at constant M_w and branching density can only be attributed to a change of polymer branching topology: as the P_E and C_M are decreased, the copolymers become more and more dendritic. The change of branching topology results from the competition between monomer insertion and chain-walking of the Pd catalyst. As was proposed previously,[2a,c] the competition between chain-walking and ethylene insertion determines the final polymer topology. As shown in Scheme 2, after ethylene or polar comonomer dissociation from the resting state S_1, the Pd catalyst isomerizes ("chain-walks")[3b,4] along the polymer chain to a certain length by β-hydride elimination and a re-addition process until it is trapped by another ethylene to go to another resting state S_2. Insertion of ethylene or polar comonomer at S_2 produces a new branch. The number of carbons (*n*) that the catalyst walks from S_1 to S_2 is the distance between two branches. The walking distance (*n*) should exhibit a statistical distribution governed by the competition between chain-walking and trapping processes. The trapping

Scheme 2. Mechanistic Model for Ethylene Copolymerization Catalyzed by the Pd-α-Diimine Catalyst[a]



[a] Individual kinetic steps are (1) dissociation of ethylene or comonomer (k_D); (2) isomerization (chain-walking, k_W); (3) association of ethylene or comonomer (trapping, k_T); and (4) insertion of ethylene or comonomer (k_{Ins}).

rate follows first-order dependence on P_E and C_M. At high P_E and C_M, the trapping is fast, and therefore the average walking distance is relatively short. The polymer formed has a relatively linear topology with moderate branches. At low P_E and C_M, the trapping is slow, and the catalyst may walk many carbons before being trapped, leading to the formation of many branches on branches, or a dendritic topology. In other words, at relatively high P_E and C_M, the insertion is more favorable so linear copolymers were formed. At very low P_E and C_M, however, the chain-walking of the Pd catalyst becomes very competitive, and copolymers with many branch-on-branches, that is, dendritic structures, were produced.

Synthesis of Functional Dendritic Copolymers. Our results have shown that by tuning copolymerization conditions, the chain-walking catalyst can be used to produce polar copolymers with controllable branching topology and comonomer incorporation level. *This provides a simple methodology for the one-pot synthesis of functional polymers with various topologies.* To show the application of this methodology, we synthesized dendritic copolymers containing multivalent functional groups including hydroxyl, epoxide, and saccharide for potential functional applications.

The hydroxyl-containing dendritic copolymers were obtained by removing the TBDPS protecting groups of the ethylene copolymers with **4** (entries 8 and 10 in Table 1). The dendritic copolymers of **4** made at low P_E and C_M were treated with tetrabutylammonium fluoride (TBAF) to give the free hydroxyl copolymers. As shown in Table 1 (entries 9 and 11), both the molecular weights and the molecular size (the radius of gyration, R_g) decrease accordingly after the deprotection. The free hydroxyl groups significantly increase the polarity of the copolymers, and the hydroxyl groups also serve as sites for further functionalization.

An epoxide-containing comonomer, **7**, was successfully copolymerized with ethylene (entry 18 in Table 1). On the basis of the structural similarity between **4** and **7** and the small R_g for the copolymer of **7**, we concluded that dendritic copolymers of **7** were formed at low P_E and C_M. The multiple epoxide groups on the copolymers serve as excellent reactive sites for further functionalization by various nucleophiles.

Finally, we synthesized dendritic copolymers having multiple saccharide groups as multivalent ligands for potential biological applications. Saccharide−protein interactions facilitate many fundamental cell−cell recognition events in processes such as host−pathogen interactions, fertilization, and the mounting of an immune response.[9] Many multivalent inhibitors including neoglycopolymers have been synthesized for biological applications.[10] Dendrimers are attractive scaffolds for constructing multivalent ligands because of their globular shape and the high local density of ligand presentation on the surface.[11] By applying our chain-walking methodology, we found that simple copolymerization of ethylene with a saccharide-containing comonomer **8** at low P_E and C_M resulted in a sugar-coated dendritic copolymer (Scheme 3).

The TMS-protected mannose comonomer **8** was synthesized according to Scheme 3.[12] Copolymerization of **8** with ethylene at low P_E and C_M yielded a sugar-containing copolymer, which upon deprotection of TMS groups afforded a mannose-functionalized copolymer (entries 19 and 20 in Table 1). On the basis of the structural similarity between comonomers **8** and **5** and the small R_g values measured by MALS, the mannose-containing copolymers should have a dendritic topology. According to previous studies by Brookhart and co-workers,[3c] functional groups usually stay at the ends of branches in polar copolymers synthesized by the Pd-bisimine catalyst due to the unique catalyst walking mechanism. Therefore, in our dendritic copolymers, the functional groups should enrich at the surface of the macromolecules because there should be more chain ends at the surface of a dendritic structure. This provides a simple one-pot synthesis to construct dendritic scaffolds to preferentially present functional groups at the surface of the macromolecules.

Conclusions

In conclusion, we have demonstrated for the first time that the branching topology of ethylene polar copolymers can be controlled by simply changing ethylene pressure and the comonomer concentrations using the Pd-bisimine chain-walking catalyst. For ethylene copolymerization with the ether and ester

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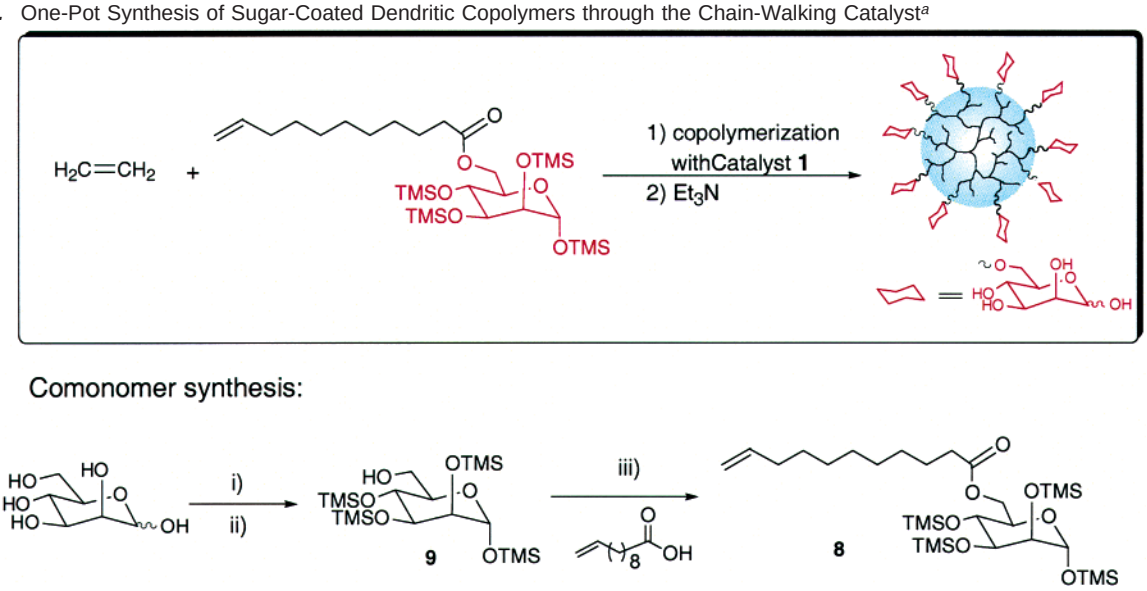
Scheme 3. One-Pot Synthesis of Sugar-Coated Dendritic Copolymers through the Chain-Walking Catalyst[a]

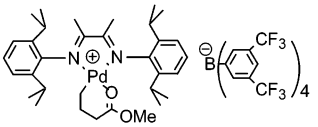


[a] Conditions: (i) TMSCl, TMSTMS, Py, 0 °C; (ii) 2% AcOH, MeOH, 0 °C, 2 h; (iii) DCC, DMAP, CH_2Cl_2.

comonomers **4**−**6**, both the incorporation ratio of the comonomers and the branching topology of the copolymers were successfully controlled by changing P_E and the comonomer concentration. The comonomer incorporation level increases linearly with the comonomer feed concentration at constant ethylene pressure. The copolymer topology becomes more dendritic as the concentrations of ethylene and comonomers are decreasing. This provides a simple route to access a wide variety of functional polymers with controllable topologies for many potential applications. As a few examples, we synthesized dendritic copolymers containing multiple hydroxyl, epoxide, and mannose groups. Although these polymers are not perfect dendrimers because of their polydisperse nature in molecular weight and branching length distribution, their branching topology and globular structure resemble those of dendrimers.[1,2] It is reasonable to expect that many chemical and physical properties of these dendritic polymers made by the chain-walking catalyst should be similar to those of dendrimers made of the same building block. Whereas perfect dendrimers have beautiful structural precision and uniformity,[1] the multistep syntheses involved in their preparations sometimes limit their general applications. Our approach offers a simple one-pot process for making functional polymers with tunable topologies starting with simple olefinic monomers. Because of the ease of synthesis and the availability of many olefinic monomers, these functional dendritic polymers may find many general applications in which polymer structural precision and uniformity are not critical. We are currently synthesizing new functional materials using the chain-walking catalysts and designing new catalysts for better catalytic properties.

Experimental Section

General Procedure. The catalyst synthesis and handling were carried out in a Vacuum Atmosphere glovebox filled with nitrogen. All other moisture- and air-sensitive reactions were carried out in flame-dried glassware using magnetic stirring under a positive pressure of argon or nitrogen. Removal of organic solvents was accomplished by rotary evaporation and is referred to as concentrated in vacuo. Flash column chromatography was performed using forced flow on EM Science 230−400 mesh silica gel. NMR spectra were recorded on Bruker DRX400, Bruker GN500, and Bruker Omega500 MHz FT-NMR instruments. Proton and carbon NMR spectra were recorded in ppm and were referenced to indicated solvents. Data were reported as follows: chemical shift, multiplicity (s = singlet, d = doublet, t = triplet, q = quartet), coupling constant(s) in hertz (Hz), and integration. Multiplets (m) were reported over the range (ppm) at which they appear at the indicated field strength. Elemental analysis was performed by Atlantic Microlabs, Atlanta, GA. Toluene, THF, diethyl ether, dichloromethane, and other solvents were purified by passing them through solvent purification columns following the method introduced by Grubbs.[13] Catalyst **1** was synthesized by following the literature report.[3b,c] The synthesis of all of the polar comonomers is described below.



Catalyst **1**

2,2-Dimethyl-pent-4-enoic Acid Methyl Ester (6).[14] To a solution of diisopropylamine (10.8 mL, 0.077 mol, 1.1 equiv) in 50 mL of dry THF was dropwise added a solution of butyllithium in cyclohexane (2.0 M, 38.5 mL, 0.077 mol, 1.1 equiv) at −78 °C. After 30 min, a solution of methyl isobutylate (8.02 mL, 0.07 mol, 1.0 equiv) in 50 mL of THF was added over 30 min at −78 °C with vigorous stirring. After 1 h, a solution of allylbromide (6.7 mL, 0.077 mol, 1.1 equiv) in 50 mL of THF was added at −78 °C. The solution was warmed to 0 °C and stirred for 30 min and then remained 2 h at room temperature. The solution was quenched with saturated NH_4Cl aqueous solution at −78 °C and extracted with hexanes (3 × 200 mL). Combined organic layers were subsequently washed with 100 mL of saturated $Na_2S_2O_3$, 100 mL of saturated $NaHCO_3$, and then 100 mL of brine. After being dried over $MgSO_4$, the solution was concentrated in vacuo to afford a yellow liquid. Vacuum distillation afforded a clear colorless liquid **6** (12.4 g, 78%). ^{1}H NMR (500 MHz, $CDCl_3$) δ: 5.70 (m, 1H), 5.00−5.05 (m, 2H), 3.65 (s, 3H), 2.27 (ddd, $J_1 = J_2 = 1.2$, $J_3 = 7.4$, 2H), 1.16 (s, 6H). ^{13}C NMR (125 MHz, $CDCl_3$) δ: 178.4, 134.7, 118.3, 52.1, 45.2, 42.8, 25.2 (2C). Anal. Calcd for $C_8H_{14}O_2$: C, 67.57; H, 9.92. Found: C, 67.45; H, 9.99.

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2,2-Dimethyl-pent-4-en-1-ol (10). To a mixture of lithium aluminum hydride (LAH) (2.6 g, 0.069 mol, 1.3 equiv) in 50 mL of dry Et_2O was added slowly a solution of **6** (7.54 g, 0.053 mol, 1.0 equiv) in 50 mL of Et_2O at 0 °C. The mixture was then heated to reflux for 3 h. At 0 °C, 20 mL of MeOH was added carefully to react with excess LAH, and then the mixture was quenched with 100 mL of 1.0 M HCl. After 300 mL Et_2O was added, the organic layer was separated, and the aqueous layer was extracted with Et_2O (3 × 150 mL). The combined organic layers were washed with 100 mL of saturated $NaHCO_3$ and 100 mL of brine, dried over $MgSO_4$, and finally concentrated in vacuo. Vacuum distillation gave a clear colorless liquid **8** (5.51 g, 91%). ^{1}H NMR (500 MHz, $CDCl_3$) δ: 5.84 (m, 1H), 5.02−5.08 (m, 2H), 3.32 (s, 2H), 2.03 (ddd, $J_1 = J_2 = 1.2$, $J_3 = 7.6$, 2H), 1.58 (m, 1H), 0.89 (s, 6H). ^{13}C NMR (125 MHz, $CDCl_3$) δ: 135.7, 117.6, 72.2, 48.6, 43.8, 35.9, 24.3 (2C). Anal. Calcd for $C_7H_{14}O$: C, 73.63; H, 12.36. Found: C, 73.51; H, 12.47.

5-Methoxy-4,4-dimethyl-pent-1-ene (3).[15] To a mixture of NaH (0.82 g, 0.034 mol, 1.1 equiv) in 100 mL of THF was dropwise added a solution of **10** (3.54 g, 0.031 mol, 1.0 equiv) in 100 mL of THF at 0 °C. After the mixture was stirred for 2 h at room temperature, a solution of MeI (4.83 g, 0.034 mol, 1.1 equiv) in 30 mL of THF was added at 0 °C. The solution was stirred at room temperature for another 2 h. After 200 mL of Et_2O followed by 200 mL of H_2O was added, the organic layer was separated, and the aqueous layer was extracted with Et_2O (3 × 100 mL). Combined organic layers were washed with 100 mL of saturated NH_4HCO_3 and 100 mL of brine, dried over $MgSO_4$, and finally concentrated in vacuo. Vacuum distillation gave a clear colorless liquid **3** (3.26 g, 82%). ^{1}H NMR (500 MHz, $CDCl_3$) δ: 5.81 (m, 1H), 5.00−5.05 (m, 2H), 3.36 (s, 2H), 3.33 (s, 3H), 2.02 (d, J = 7.5, 2H), 1.57 (m, 2H), 1.30 (s, 6H). ^{13}C NMR (125 MHz, $CDCl_3$) δ: 135.8, 117.1, 82.0, 59.5, 43.9, 31.8, 24.6, 23.3. Anal. Calcd for $C_8H_{16}O$: C, 74.94; H, 12.58. Found: C, 74.84; H, 12.62.

10-Methoxy-dec-1-ene (2).[15] Referring to the preparation of methyl ether **3**, we found that using dec-9-en-1-ol (4.84 g, 0.031 mol, 1.0 equiv) afforded **2** as colorless liquid (4.86 g, 93%). ^{1}H NMR (500 MHz, $CDCl_3$) δ: 5.81 (dddd, $J_1 = J_2 = 6.7$, $J_3 = 10.4$, $J_4 = 17.1$, 1H), 4.99 (dddd, $J_1 = J_2 = 1.6$, $J_3 = 2.2$, $J_4 = 17.1$, 1H), 4.93 (dddd, $J_1 = J_2 = 1.3$, $J_3 = 2.2$, $J_4 = 10.2$, 1H), 3.36 (t, $J = 3.4$, 2H), 3.33 (s, 3H), 2.03 (m, 2H), 1.57 (m, 2H), 1.30 (m, 10H). ^{13}C NMR (125 MHz, $CDCl_3$) δ: 140.3, 114.6, 73.4, 61.0, 34.3, 30.1, 29.9, 29.8, 29.5, 29.3, 26.6. Anal. Calcd for $C_{11}H_{22}O$: C, 77.58; H, 13.02. Found: C, 77.41; H, 13.22.

***tert*-Butyl-(2,2-dimethyl-pent-4-enyloxy)-diphenyl-silane (4).**[16] To a mixture of imidazole (2.54 g, 0.037 mol, 1.2 equiv) and **10** (3.54 g, 0.031 mol, 1.0 equiv) in 100 mL of CH_2Cl_2 was slowly added a solution of *tert*-butylchlorodiphenylsilane (10.17 g, 0.037 mol, 1.2 equiv) in 40 mL of CH_2Cl_2 at 0 °C. After the mixture was stirred overnight at room temperature, water was added, and the organic layer was washed with water twice and dried over $MgSO_4$. The solution was concentrated in vacuo and purified by column chromatography (1:99/ethyl acetate: hexanes) to afford colorless oil **4** (8.96 g, 82%). ^{1}H NMR (500 MHz, $CDCl_3$) δ: 7.73 (m, 4H), 7.44 (m, 6H), 5.86 (m, 1H), 5.03−5.10 (m, 2H), 3.37 (s, 2H), 2.13 (ddd, $J_1 = J_2 = 1.4$, $J_3 = 8.0$, 2H), 1.14 (s, 9H), 0.94 (s, 6H). ^{13}C NMR (125 MHz, $CDCl_3$) δ: 135.9, 135.7 (2C), 134.1 (4C), 129.7 (4C), 127.8 (2C), 117.1, 72.3, 43.5, 36.2, 27.1, 24.3 (2C), 19.7 (3C). Anal. Calcd for $C_{23}H_{32}OSi$: C, 78.35; H, 9.15; O, 4.54. Found: C, 78.31; H, 9.20; O, 4.59.

2-(1,1-Dimethyl-but-3-enyl)-oxirane (7).[17] To a solution of oxalyl chloride (8.38 g, 0.066 mol, 1.1 equiv) in 100 mL of CH_2Cl_2 was dropwise added DMSO (16.6 g, 0.132 mol, 2.2 equiv) solution in 50 mL of CH_2Cl_2 at −78 °C. After the mixture was stirred for 0.5 h, a solution of **10** (11.9 g, 0.06 mol, 1.0 equiv) in 50 mL of CH_2Cl_2 was dropwise added over 0.5 h at −78 °C. After 0.5 h, Et_3N (30.36 g, 0.30 mol, 5.0 equiv) was dropwise added to the reaction mixture at −78 °C. After another 0.5 h, the reaction mixture was allowed to warm to room temperature. After 1 h, 300 mL of H_2O was added. The organic layer was separated, and the aqueous layer was extracted with CH_2Cl_2 (2 × 150 mL). Combined organic layers were washed with saturated NaCl solution (3 × 150 mL), dried over $MgSO_4$, and finally concentrated in vacuo to afford a yellow liquid. Vacuum distillation afforded a clear colorless liquid, 2,2-dimethyl-pent-4-enal, **11** (9.0 g, 76%), which was used in the next step of the synthesis. In a N_2 glovebox, NaH (0.26 g, 0.011 mol, 1.1 equiv) was suspended in 10 mL of anhydrous THF. To this stirring mixture was added trimethylsulfoxonium chloride (1.41 g, 0.011 mol, 1.1 equiv). The mixture was brought to gentle reflux for 2 h. After the mixture was cooled to 55 °C, **11** (1.26 g, 0.01 mol, 1.0 equiv) in 10 mL of THF was added slowly into the above mixture over 1.5 h. The solution was stirred at 55 °C for another 1.5 h, and then at room temperature overnight. After the solvent was removed to half volume, water and pentane were added to the mixture. The pentane layer was separated, washed twice with water, dried over anhydrous Na_2SO_4, and finally concentrated in vacuo to afford a nearly colorless oil. The product was purified by passing it through a short silica column with EtOAc/hexanes (1:30) as eluent to yield colorless oil **7** (60%). ^{1}H NMR (500 MHz, $CDCl_3$) δ: 5.84 (dddd, $J_1 = J_2 = 7.5$, $J_3 = 10.6$, $J_4 = 16.5$, 1H), 5.02−5.08 (m, 2H), 2.77 (dd, $J_1 = 2.9$, $J_2 = 4.1$, 1H), 2.63 (dd, $J_1 = 4.1$, $J_2 = 4.7$, 1H), 2.60 (dd, $J_1 = 2.9$, $J_2 = 4.7$, 1H), 2.08 (m, 2H), 1.28 (m, 2H), 0.88 (s, 3H), 0.84 (s, 3H). ^{13}C NMR (125 MHz, $CDCl_3$) δ: 134.9, 118.0, 77.5, 59.7, 45.1, 44.4, 23.6, 22.5. Anal. Calcd for $C_8H_{14}O$: C, 76.14; H, 11.18. Found: C, 76.10; H, 11.24.

Undec-10-enoic Acid 3,4,5,6-Tetrakis-trimethylsilanyloxy-tetrahydro-pyran-2-ylmethyl Ester (8). The TMS-protected mannose, **9**, was prepared according to the literature procedure.[12] To a solution of **9** (37.5 g, 0.08 mol) in dichloromethane (400 mL) were added 10-undecenoic acid (16.2 g, 0.088 mol), 4-(dimethylamino)pyridine (DMAP) (0.69 g, 0.0056 mol), and 1,3-dichlorohexylcarbodiimide (DCC) (18.99 g, 0.092 mol) at 0 °C. The mixture was kept stirring for 1 h at room temperature and then filtered through Celite. The filtrate was diluted with dichloromethane and washed with dilute acetic acid (5%) and water, dried over Na_2SO_4, and concentrated in vacuo. Flash chromatography (gradient eluent 0−5% ethyl acetate in hexanes) of the residue gave **8** as oil (30.5 g, 60%). ^{1}H NMR (500 MHz, $CDCl_3$) δ: 5.77−5.85 (m, 1H), 4.92−5.01 (m, 2H), 4.35 (dd, $J_1 = 2.0$, $J_2 = 11.7$, 1H), 4.05 (dd, $J_1 = 5.8$, $J_2 = 11.7$, 1H), 3.84−3.89 (m, 3H), 2.32−2.35 (m, 2H), 2.04 (dd, $J_1 = 7.0$, $J_2 = 14.4$, 2H), 1.27−1.38 (m, 14H), 0.17 (s, 9H), 0.16 (s, 9H), 0.14 (s, 9H), 0.13 (s, 9H). ^{13}C NMR (125 MHz, $CDCl_3$) δ: 174.0, 139.4, 114.3, 95.08, 75.3, 72.2, 72.0, 68.7, 64.1, 34.9, 34.0, 31.8, 29.5, 29.4, 29.4, 29.3, 29.1, 25.0, 22.9, 14.3, 0.9 (3C), 0.8 (3C), 0.5 (3C), 0.1 (3C). Anal. Calcd for $C_{29}H_{62}O_7Si_4$: C, 54.84; H, 9.84; Si, 17.69. Found: C, 54.99; H, 9.76; Si, 17.59.

Polymerization Procedure. Ethylene homopolymerization and copolymerization with polar comonomers were performed in a Parr pressure reactor equipped with a mechanical stirrer and a temperature controller. A typical polymerization procedure is described as follows: The Parr reactor was preheated to 100 °C for 2 h under vacuum and then cooled under N_2 to room temperature before use. A comonomer solution in chlorobenzene/toluene (1:3) was degassed and then added into a preprepared catalyst **1** solution in chlorobenzene/toluene (1:3). The whole mixture was transferred into the Parr reactor under N_2. After the reactor was purged with N_2 and ethylene, the system was filled with ethylene to the desired pressure, and polymerization was allowed to continue at room temperature for about 1−2 days. The polymerization was quenched by addition of an excess amount of triethylsilane under N_2. The polymer solution was passed through Celite and neutral alumina gel to remove residual catalyst, and then concen-

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trated in vacuo. The polymer was finally precipitated out from methanol or acetone and dried under vacuum.

Deprotection of TBDPS and TMS. For ethylene copolymers with the comonomer **4** and **8**, after obtaining the copolymers, the TBDPS or TMS protection group was removed to free all of the hydroxyl groups. The deprotection of TBDPS was done by treating the copolymers with tetrabutylammonium fluoride (5.0 equiv of the calculated TBDPS group).[18] One example is shown here for an ethylene copolymer with **4** (0.1 atm and 9.1% comonomer incorporation ratio): The copolymer (2.0 g, OTBDPS: 3.15 mmol, 1.0 equiv) was dissolved in 100 mL of THF. Tertrabutylammonium fluoride (15.7 mL of a 1.00 M solution in THF, 15.7 mmol, 5.0 equiv) was slowly added into the copolymer solution. The solution was then brought to gentle reflux for 48 h. After being concentrated in vacuo, the mixture was partitioned between toluene and water. The organic layer was separated, washed twice with water, dried over $MgSO_4$, and concentrated in vacuo. The product was then precipitated out by adding a large amount of methanol, and dried under vacuum. The deprotection of TMS was done by treatment with Et_3N.

NMR Characterization of Copolymers. The chemical structures of the copolymers were analyzed by ^{1}H NMR spectra. The polar comonomer incorporation ratio was calculated from the integrations of peaks of the comonomer and peaks of the polyethylene backbone. The calculation of branching density was based on the integration of the terminal methyl group and the integration of the polyethylene backbone. The ^{1}H NMR (500 MHz, $CDCl_3$) data for all of the copolymers are summarized here. Ethylene-**3** copolymer δ: 3.37, 3.34, 1.05−1.40 (broad), 0.80−0.92 (broad). Ethylene-**4** copolymer δ: 7.55−7.75, 7.30−7.40, 3.29, 1.08−1.40 (broad), 1.06, 0.80−0.92 (broad). Ethylene-**4** copolymer after deprotection of TBDPS δ: 3.30, 1.08−1.40 (broad), 0.80−0.92 (broad). Ethylene-**5** copolymer δ: 3.67, 2.35, 1.05−1.40 (broad), 0.80−0.92 (broad). Ethylene-**6** copolymer δ: 3.67, 1.05−1.40 (broad), 0.80−0.92 (broad). Ethylene-**7** copolymer δ: 2.74, 2.63, 2.59, 1.05−1.40 (broad), 0.80−0.92 (broad). Ethylene-**8** copolymer δ: 4.35, 4.05, 3.89, 3.84, 2.33, 2.04, 1.05−1.40 (broad), 0.80−0.92 (broad), 0.09−0.16. Ethylene-**8** copolymer after deprotection of TMS δ: 2.58−5.35 (broad, m), 2.04, 1.04−1.40 (broad), 0.81−0.93 (broad).

SEC-MALS Characterization of Copolymers.[2a,e] All of the polymers were characterized by size-exclusion chromatography (SEC) coupled to a multi-angle light-scattering detector (MALS) for obtaining both the molecular weight (M) and the radius of gyration (R_g). Measurements were made on highly dilute fractions eluting from a SEC consisting of a HP Aglient 1100 solvent delivery system/autoinjector with an online solvent degasser, temperature-controlled column compartment, and an Aglient 1100 differential refractometer. A Dawn DSP 18-angle light-scattering detector (Wyatt Technology, Santa Barbara, CA) was coupled to the SEC to measure both the molecular weights and the sizes for each fraction of the polymer eluted from the SEC column. A 30 cm column was used (Polymer Laboratories PLgel Mixed C, 5 μm particle size) to separate polymer samples. The mobile phase was tetrahydrofuran (THF), and the flow rate was 0.5 mL/min. Both the column and the differential refractometer were held at 35 °C. Next, 60 μL of a 2 mg/mL solution was injected into the column. ASTRA 4.7 from Wyatt Technology was used to acquire data from the 18 scattering angles (detectors) and the differential refractometer. The M_w, M_n, R_g data were obtained by following classical light-scattering treatments. The R_g data reported are the weight-averaged values.

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