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Cobalt(III)-Catalyzed Living Polymerization of Ethylene: Routes to End-Capped Polyethylene with a Narrow Molar Mass Distribution

M. Brookhart,* J. M. DeSimone, B. E. Grant, and M. J. Tanner

Department of Chemistry, University of North Carolina at Chapel Hill, Chapel Hill, North Carolina 27599-3290

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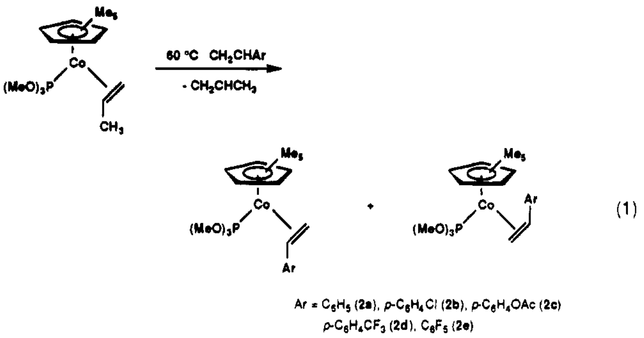
The end groups of polymer chains often play a significant role in determining the processing and performance characteristics of a polymeric material. Appropriate functional groups on the terminal position can allow the incorporation of these units into new materials to form block, segmented, or graft copolymers. In addition, these end groups can influence the orientation (e.g., surface segregation) of polymer chains and can provide ways for altering polymers to modify adhesion, melt and solution rheology, and dyeability. Living anionic polymerization methods have provided perhaps the most important route to control end groups for polymers made by a chain-growth polymerization process[1–6] but are limited in scope to certain monomers.

Introduction of functional groups into polyolefins has been particularly difficult due to the incompatibility of such groups with catalyst systems normally used to polymerize hydrocarbon-based olefins.[7,8] With respect to end-capped polyethylenes, Bergbreiter[9] has developed living, anionic polymerization methods for the preparation of various terminally functionalized low molecular weight (1800–2500) materials. Yasuda[10] has used organolanthanide complexes to carry out the synthesis of block copolymers of ethylene and MMA. In this paper we report the use of living Co(III)-catalyzed polymerizations of ethylene to prepare a variety of end-functionalized polyethylenes.

The previously reported Co(III) complexes, which can be used to initiate living polymerization of ethylene, have the general structure $[C_5Me_5P(OMe)_3CoCH_2CHR\text{-}\mu\text{-}H]^+$ (**1**; R = H, alkyl).[11] The strategies we describe here for the synthesis of controlled molar mass, end-functionalized polyethylenes employ analogs of **1**, where R now possesses a functional group, to initiate ethylene polymerization.

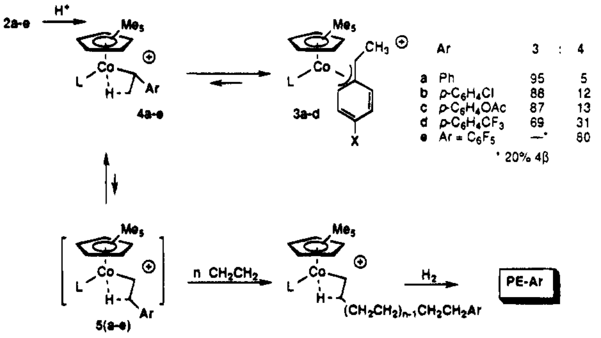
In preparing these compounds, two salient features of this family of compounds were considered: (1) facile chain migration of higher *n*-alkyl and cycloalkyl analogs of **1** has been observed; (2) functional group interaction with the highly electrophilic metal center would likely lead to catalyst deactivation. Thus, derivatives of **1** have been prepared in which interaction between the electrophilic metal and the appended functional group has been blocked, and catalytic activity is thereby maintained.

The first of these methodologies relies on the presence of an aryl group to block migration of the metal alkyl chain, thus allowing functional groups to be appended to the aryl end group. Synthesis of the catalyst precursors involved thermal substitution of a labile propene complex with various styrenes, which gives two isomeric products[12] differing in olefin orientation (eq 1).



Protonation of styrene complexes **2a–e** with $HBAr'_4{\cdot}2Et_2O$ ($Ar' = 3,5\text{-}(CF_3)_2C_6H_3$)[13] gave an equilibrating mixture of isomers. As illustrated in Scheme 1, these products include η^3-benzyl complexes **3a–d** and α-aryl-substituted, β-agostic complexes **4a–e**. Isomers **3a–d** and **4a–e** were characterized by low-temperature NMR spectroscopic techniques.[14] The observed isomeric ratios (3:4) at −40 °C ranged from 20:1 (X = H) to 2:1 (X = CF_3). In the case of Ar = C_6F_5, an η^3-benzyl species was not detected; **4e** was the major species, and a β-aryl substituted agostic isomer **5e** was the minor (20%) species. Exposing chlorobenzene solutions of these complexes to 1 atm of ethylene for 3 h, followed by hydrogenolysis[15] of the Co–alkyl bond, led to the recovery of polyethylene. Gel permeation chromatographic analysis of polymers prepared by this procedure showed very narrow molar mass distributions (M_w/M_n = 1.11–1.16) up to at least 2.0 × 10^4, indicative of a living polymerization system. Results employing complexes **4a–e** are summarized in Table 1. ^{13}C NMR spectra of the polymers[16] both confirmed the presence of the aryl end group and established strict polymer linearity. A single methyl resonance was observed (δ = 15.1 ppm), indicating that the active initiating species toward insertion in Scheme 1 are β-aryl-substituted, β-agostic isomers **5a–e** (i.e., if **4a–e** were the initiating species the resulting polymer, $CH_3CH_2(CH_2CH_2)_nCH(CH_3)Ar$, would exhibit two methyl resonances).

Scheme 1



In the second methodology, migration along the alkyl chain is blocked by a silyl group. We have previously reported the ability of **1** to function as an α-olefin hydrosilation catalyst.[17] The mechanism has been extensively investigated and is illustrated in Scheme 2. Exposure of **1** to silane leads to reductive elimination of ethane (step i) and formation of a 16e Co–silyl complex, which binds and inserts olefin (step ii) to give the catalyst resting state **5a**. A series of reversible β-elimination and readdition steps (step iii) leads to isomer **5b**, which is observed by NMR spectroscopy *only* when the silane concentration becomes depleted and cleavage of the Co–alkyl bond to reenter the catalytic cycle (step iv) can no longer occur. Thus, silyl-substituted Co–alkyl species **5b** can be generated under

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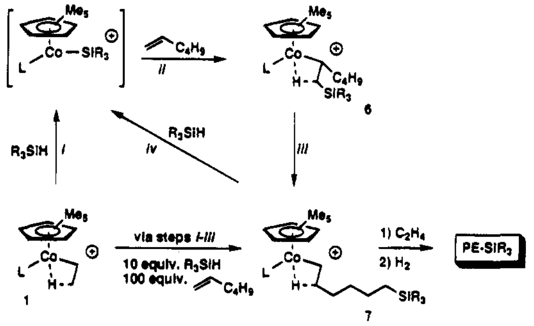
Table 1

end group	yield (g)	M_n (×10^{-4})	M_w (×10^{-4})	MWD
$-H$	0.600	1.61	1.84	1.14
$-C_6H_5$	0.418	1.57	1.82	1.16
$-C_6H_4Cl$	0.438	1.44	1.60	1.11
$-C_6H_4CF_3$	0.459	1.48	1.65	1.11
$-C_6H_4OAc$	0.813	2.12	2.62	1.16
$-C_6F_5$	0.650	1.93	2.25	1.16
$-SiEt_3$	0.477	1.61	1.86	1.15
$-H^a$	0.507	1.06	1.24	1.17
$-SiMe_2Cl^{a,b}$	0.620	1.02	1.45	1.41

[a] All samples run with 50 mg (0.04 mmol) of catalyst, under 1 atm of ethylene, in chlorobenzene for 3 h except *a*, in methylene chloride for 6 h. [b] Collected as PE-Si(Me)$_2$OEt.

Scheme 2



conditions of silane depletion. The agostic structure suggests that **5b**, like the Co–ethyl species **1**, should serve as an ethylene polymerization catalyst.[18] Indeed, following this strategy to generate species **5b** and then exposing to ethylene and cleaving the Co–alkyl bond with hydrogen, we have produced silyl-functionalized PE of low polydispersity, and in yields comparable to those obtained using complex **1** (Table 1).[19]

The chlorosilane $Me_2(Cl)SiH$ has also been used, but the extreme sensitivity of the highly electrophilic Co(III) system to the halide ion, readily formed by attack of water on silyl chlorides, necessitates scrupulously dry working conditions. NMR spectra,[19] yields, and polydispersities[20] (Table 1) of polymer samples obtained indicate that under such conditions the system provides a viable route to end-functionalized PE.

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Supporting Information Available: Experimental data for the synthesis and characterization of catalyst initiating species, polymerization conditions, and polymer characterization (8 pages). Ordering information is given on any current masthead page.

References and Notes

(1) Morton, M. *Anionic Polymerization: Principles and Practice*; Academic Press: New York, 1983.

(2) Bates, F. S. *Science* **1991**, *251*, 898.

(3) Webster, O. W. *Science* **1991**, *251*, 887.

(4) Young, R. N.; Quirk, R. P.; Fetters, L. *Adv. Polym. Sci.* **1984**, *56*, 70.

(5) Schulz, D. N.; Halasa, A. F. *J. Polym. Sci., Polym. Chem. Ed.* **1977**, *15*, 2401.

(6) Peters, M. A.; Belu, A. M.; Linton, R. W.; Dupray, L.; Meyer, T. J.; DeSimone, J. M. *J. Am. Chem. Soc.* **1995**, *117*, 3380.

(7) Chung has reported the use of protected monomers which are compatible with Ziegler–Natta catalysts. See, for example: (a) Chung, T. C. *Macromolecules* **1988**, *21*, 865. (b) Ramakrishnan, S.; Berluche, E.; Chung, T. C. *Macromolecules* **1990**, *23*, 378.

(8) Waymouth has reported that certain functionalized α,ω-dienes are compatible with d^0 early metal catalysts used for cyclopolymerization: Kesti, M. R.; Coates, G. W.; Waymouth, R. M. *J. Am. Chem. Soc.* **1992**, *114*, 9679.

(9) (a) Bergbreiter, D. E.; Chandran, R. *J. Am. Chem. Soc.* **1987**, *109*, 174. (b) Bergbreiter, D. E.; Chandran, R. *J. Chem. Soc., Chem. Commun.* **1985**, 1396. (c) Bergbreiter, D. E.; Blanton, J. R. *J. Chem. Soc., Chem. Commun.* **1985**, 337. (d) Bergbreiter, D. E.; Hein, M. D. *Macromolecules* **1990**, *23*, 764. For related work, see: Crassous, G.; Abadie, M.; Schue, F. *Eur. Polym. J.* **1979**, *15*, 757.

(10) Yasuda, X.; Furo, M.; Yamamoto, H. *Macromolecules* **1992**, *25*, 5115.

(11) (a) Schmidt, G. F.; Brookhart, M. *J. Am. Chem. Soc.* **1985**, *107*, 1443. (b) Brookhart, M.; Volpe, A. F., Jr.; Lincoln, D. M.; Horvath, I. T.; Millar, J. M. *J. Am. Chem. Soc.* **1990**, *112* , 5634. (c) Brookhart, M.; Volpe, A. F., Jr.; DeSimone, J.; Lamanna, W. M. *Polym. Prepr. (Am Chem. Soc., Div. Polym. Chem.)* **1991**, *32*, 461. (d) The living nature of the polymerization has been confirmed by spectroscopic characterization of initiating and propagating (*i.e.*, resting state) species[11a–c] and by linear plots of M_n versus conversion: Volpe, A. F., Jr. PhD Dissertation, University of North Carolina at Chapel Hill, 1991. (e) For a recent report of a Nb-based living ethylene polymerization catalyst, see: Mashima, K.; Fujikawa, S.; Urata, H.; Tanaka, E.; Nakamura, A. *J. Chem. Soc., Chem. Commun.* **1994**, 1623.

(12) Procedure for **2a**: 100 mg of $Cp^*\{P(OMe)_3\}Co(CH_2CHMe)$ (0.278 mmol) and 0.035 mL of styrene (0.306 mmol, 1.1 equiv) were dissolved in 10 mL of hexane in a Kontes flask. The flask was sealed under vacuum and heated to 60 °C for 2 h. The solution was filtered, concentrated to 1 mL, and chilled to −78 °C to give **2a** as dark red crystals: 102 mg, 87%. **2a** (major isomer 87%): ^1H NMR δ 7.00−7.35 (m, 5 H, Ph), 2.96 (d, 9 H, J_{HP} = 10.8 Hz, $P(OMe)_3$), 3.14 (ddd, 1 H, J_{HH} = 11.7, 8.4 Hz, J_{HP} = 1.5 Hz, $PhC\mathit{H}CH_2$), 2.01 (td, 1 H, J_{HH} = 11.7, 1.5 Hz, J_{HP} = 11.7, *trans*-$PhCHCH_2$), 1.67 (d, 15 H, J_{HP} = 2.0 Hz, Cp*), 1.64 (dt, 1 H, J_{HH} = 8.4, 1.5 Hz, J_{HP} = 1.5 Hz, *cis*-$PhCHCH_2$); ^{13}C NMR δ 149.8 (d, J_{CP} = 2.7 Hz, *i*-C), 127.7 (*o*- or *m*-C), 127.6 (*o*- or *m*-C), 123.0 (*p*-C), 91.8 (d, J_{CP} = 3.0 Hz, C_5Me_5), 49.1 ($P(OMe)_3$), 48.2 (CHPh), 28.5 (d, J_{CP} = 8.4 Hz, CH_2), 9.9 ($C_5\mathit{Me}_5$). **2a** (minor isomer 13%): ^1H NMR δ 7.00−7.30 (m, 5 H, Ph), 3.29 (d, 9 H, J_{HP} = 12.3 Hz, $P(OMe)_3$), 3.52 (m,1 H, $PhC\mathit{H}CH_2$), 1.92 (m, 1H, $PhCHC\mathit{H}_2$), 1.48 (d, 15 H, J_{HP} = 2.1 Hz, Cp*), remaining styrene signal obscured; ^{13}C NMR δ 148.4 (*i*-C), 128.7 (*o*- or *m*-C), 127.9 (*o*- or *m*-C), 123.4 (*p*-C), 91.7 (d, J_{CP} = 3.0 Hz, C_5Me_5), 49.9 ($P(OMe)_3$), 45.9 (d, J_{CP} = 6.4 Hz, CHPh), 24.8 (d, J_{CP} = 6.9 Hz, CH_2) 10.0 ($C_5\mathit{Me}_5$). Anal. Calcd for $C_{21}H_{32}O_3CoP$: C, 59.71; H, 7.64. Found: C, 59.86; H, 7.07. Full spectral and analytical data for complexes **2a–e** are given as supporting information.

(13) (a) The advantages of using the nonnucleophilic $BAr_4'^-$ counterion to stabilize cationic Co(III) complexes have been reported: Brookhart, M.; Grant, B.; Volpe, A. F., Jr. *J. Am. Chem. Soc.* **1992**, *11*, 3920. (b) Synthesis of $HBAr_4'$ has also been reported: Taube, R.; Wache, S. *J. Organomet. Chem.* **1992**, *428*, 431.

(14) Procedure for **3a**: 90 mg (0.21 mmol) of $Cp^*[P(OMe)_3]Co(CH_2CHPh)$ (**2a**) and 216 mg of $HBAr'_4\cdot 2Et_2O$ were dissolved in 0.5 mL of CH_2Cl_2 at 0 °C. The resultant deep green solution was cooled to −78 °C, at which point precipitation began. Hexane (5 mL) was slowly added until precipitation was complete. The dark green solid was rinsed with cold hexane (2 × 2 mL), dried under reduced pressure, and collected: 236 mg, 86%. **3a**: ^1H NMR δ 7.89 (m, 1 H, Hx), 7.63 (m, 1 H, H_1), 7.63 (m, 1 H, H_2), 7.00 (m, 1 H, H_3), 4.15 (t, 1 H, J_{HH} = 6.1 Hz, H_4), 3.81 (d, 9 H, J_{HP} = 10.6 Hz, $P(OMe)_3$), 1.83 (dq, 1 H, J_{HP} = 16.3 Hz, J_{HH} = 6.7 Hz, H_5), 1.73 (dd, 3 H, J_{HH} = 6.7 Hz, J_{HP} = 1.9 Hz, CH_3), 1.17 (d, 15 H, J_{HP} = 2.2 Hz, Cp*); ^{13}C NMR δ 133.3, 132.9, 130.4 125.8 (C_1, C_2, C_3, Cx), 100.5 (C_5), 95.2 (C_5Me_5), 74.5 (C_4), 53.7 (d, J_{CP} obscured by solvent signal, $P(OMe)_3$), 45.0 (d, J_{CP} = 14.0 Hz, C_6), 15.9 (CH_3), 8.1 (C_5Me_5). **4a**: ^1H NMR δ 7.10−7.40 (m, 5 H, Ph), 4.65 (br m, 1 H, H_α), 3.20 (d, 9 H, J_{HP} = 11.7 Hz, P(OMe)3), 1.67 (d, 15 H, J_{HP} = 2.2 Hz, Cp*), 0.32 (br, 1 H, H_β), −0.21 (br, 1 H, H_β), −11.91 (m, 1 H, μ-H). Anal. Calcd for $C_{53}H_{45}O_3CoBF_{24}P$: C, 49.48; H, 3.53. Found: C, 49.95; H, 3.41. Full spectral and analytical data for complexes **3a–d** and **4a–e** are given as supporting information.

Assignment of agostic structures **4a–e** was based on analogy to previously reported agostic alkyl complexes: Brookhart, M.; Lincoln, D. L.; Volpe, A. F., Jr.; Schmidt, G. F. *Organometallics* **1989**, *8*, 1212. See also ref 11.

(15) The organometallic products of this and related reactions will be reported in a future publicaton: Brookhart, M.; Grant, B., manuscript in preparation.

(16) ^{13}C NMR spectra were recorded for polymer samples prepared during a 30-min reaction time, corresponding to $M_n = 2.7 \times 10^3$ (based on a turnover rate of approximately 3.2 TO/min). ^{13}C NMR data for these polymers are given as supporting information.

(17) Brookhart, M.; Grant, B. *J. Am. Chem. Soc.* **1993**, *115*, 2151.

(18) In previous papers we have addressed the implications of an agostic structure in ethylene-polymerizing, electrophilic metal–alkyl complexes: see ref 11.

(19) The presence of silyl end groups was verified by ^{13}C NMR spectra of the polymers, again by analyzing samples prepared during a 30-min reaction time. These data are given as supporting information.

(20) The somewhat broader polydispersities of the Me_2SiCl-end-capped samples can be attributed to partial catalyst poisoning from Cl^-. This is consistent with our previous observations that cationic Co(III)–silyl species are extremely moisture sensitive: see ref 17.

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