Homogeneous Ziegler–Natta Polymerization of Functionalized Monomers Catalyzed by Cationic Group IV Metallocenes

Michael R. Kesti, Geoffrey W. Coates, and Robert M. Waymouth*

Department of Chemistry
Stanford University
Stanford, California 94305
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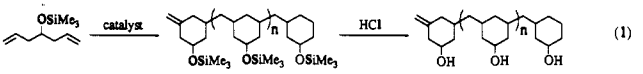
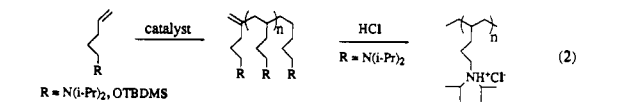
Ziegler–Natta catalysts are remarkable in their ability to polymerize α-olefins to high molecular weight, stereoregular polyolefins.[1-4] One of the major limitations of conventional Ziegler–Natta catalysts is their intolerance to Lewis bases; catalysts based on titanium halides and alkylaluminum cocatalysts are poisoned by most types of monomers containing ethers, esters, amines, and carboxylic acids.[1,5] The absence of functionality in hydrocarbon polymers seriously affects their adhesive properties, affinity for dyes, permeability, and compatibility with more polar polymers. Previous attempts[6] to polymerize sterically hindered amines,[7,8] esters and amides,[9-11] alkyl halides,[12] and carboxylic acids[13] using catalysts derived from $TiCl_3$ and $AlR_{3-n}Cl_n$ have achieved limited success due to the severe loss of catalytic activity in the presence of these monomers.[14]

The recent development[15-20] of cationic, group 4 metallocene catalysts provides one solution to this long-standing problem.[21] These catalysts have been shown to polymerize olefins in the *absence* of alkylaluminum cocatalysts in solvents such as anisole, *N,N*-dimethylaniline, and chlorobenzene.[18d,f] Herein, we report that cationic, group 4 metallocenes are active catalysts for the *homopolymerization* of α-olefins containing silyl-protected alcohols and tertiary amines.

Catalysts derived from the reaction of $Cp^*_2ZrMe_2$ with $B(C_6F_5)_3$ or [*N,N*-dimethylanilinium]$[B(C_6F_5)_4]$ (denoted as $[Cp^*_2ZrMe]^+X^-$, Cp^* = pentamethylcyclopentadienyl, X = $B(C_6F_5)_4$ or $CH_3B(C_6F_5)_3$)[16,17,19] are active for the polymerization of the functionalized diene and α-olefins 4-TMSO-1,6-heptadiene (TMSO = trimethylsiloxy), 5-TBDMSO-1-pentene (TBDMSO = *tert*-butyldimethylsiloxy), and 5-(*N,N*-diisopropylamino)-1-pentene (eqs 1 and 2, Table I).[22] Cyclopolymerization[23] of



(1)



(2)

4-TMSO-1,6-heptadiene occurs rapidly at room temperature in the presence of $[Cp^*_2ZrMe]^+X^-$ (eq 2, average activity[24] at 37% conversion = 720 turnovers/h, >250 turnovers, Table I, entry 1) to yield poly(methylene-3,5-(1-TMSO)cyclohexanediyl). End-group analysis of the polymer by ^1H and ^{13}C NMR reveals methylenecyclohexane and cyclohexane end groups, indicative of chain transfer via β-H elimination. As for 1-hexene, low molecular weight oligomers are obtained at room temperature;[25] higher molecular weights are observed at lower reaction temperatures. Higher molecular weight poly(methylene-3,5-(1-TMSO)cyclohexanediyl) (M_n = 46000, M_w/M_n = 3.1, 38% yield[26]) is obtained from the reaction of $[Cp^*_2HfMe]^+X^-$ in *neat* monomer at −25 °C. Complete cyclization was observed as no unsaturation was detected by ^1H NMR.

The chiral $[(EBTHI)ZrMe]^+X^-$ catalysts (EBTHI = ethylene-1,2-bis(η^5-4,5,6,7-tetrahydro-1-indenyl)) are more easily poisoned by silyl ethers as compared to the $[Cp^*_2ZrMe]^+X^-$

(1) Boor, J., Jr. *Ziegler–Natta Catalysts and Polymerizations*; Academic Press: New York, 1979.
(2) (a) Ewen, J. A. *J. Am. Chem. Soc.* **1984**, *106*, 6355. (b) Ewen, J. A.; Haspeslagh, L.; Atwood, J. L.; Zhang, H. *J. Am. Chem. Soc.* **1987**, *109*, 6544. (c) Ewen, J. A.; Jones, R. L.; Razavi, A.; Ferrara, J. D. *J. Am. Chem. Soc.* **1988**, *110*, 6255.
(3) (a) Kaminsky, W.; Kulper, K.; Brintzinger, H. H.; Wild, F. R. W. P. *Angew. Chem., Int. Ed. Engl.* **1985**, *24*, 507. (b) Kaminsky, W.; Spiehl, R. *Makromol. Chem.* **1989**, *190*, 515.
(4) (a) Pino, P.; Cioni, P.; Galimberti, M.; Wei, J.; Piccolrovazzi, N. In *Transition Metals and Organometallics as Catalysts for Olefin Polymerization*; Kamisky, W., Sinn, H., Eds.; Springer-Verlag: New York, 1988; p 269. (b) Pino, P.; Cioni, P.; Wei, J. *J. Am. Chem. Soc.* **1987**, *109*, 6189.
(5) Polymerization of borane monomers has been investigated recently by Chung: (a) Chung, T. C. *Macromolecules* **1988**, *21*, 865. (b) Ramakrishnan, S.; Berluche, E.; Chung, T. C. *Macromolecules* **1990**, *23*, 378. (c) Chung, T. C. *Chemtech* **1991**, *21*, 496. (d) Chung, T. C. *J. Inorg. Organomet. Polym.* **1991**, *1*, 37.
(6) Padwa, A. R. *Prog. Polym. Sci.* **1989**, *14*, 811.
(7) Homopolymerization of amines and silyl ethers: Giannini, U.; Bruckner, G.; Pellino, E.; Cassata, A. *J. Polym. Sci., Part C* **1968**, *22*, 157.
(8) Copolymerizations of hindered piperidines with propylene: Wilén, C. E.; Auer, M.; Näsman, J. H. *J. Polym. Sci., Part A: Polym. Chem.* **1992**, *30*, 1163.
(9) Polymerization of esters: (a) Purgett, M. D. Ph.D. Thesis, University of Massachusetts, 1984. (b) Vogl, O. *J. Macromol. Sci., Chem.* **1985**, *A22* (5–7), 541. (c) Purgett, M. D.; Macknight, W. J.; Vogl, O. *Polym. Eng. Sci.* **1987**, *27*, 1461. (d) Purgett, M. D.; Vogl, O. *J. Polym. Sci., Part A: Polym. Chem.* **1988**, *26*, 677. (e) Purgett, M. D.; Vogl, O. *J. Polym. Sci., Part A: Polym. Chem.* **1989**, *27*, 2051. (f) Landoll, L. M.; Breslow, D. S. *J. Polym. Sci., Part A: Polym. Chem.* **1989**, *27*, 2189.
(10) (a) Schulz, D. N.; Kitano, K.; Burkhardt, T. J.; Langer, A. W. U.S. Patent 4518757, 1984. (b) Schulz, D. N.; Bock, J. *J. Macromol. Sci., Chem.* **1991**, *A28* (11–12), 1235.
(11) (a) Clark, K. J. U.S. Patent 3492277, 1970. (b) Holler, H. V.; Youngman, E. A. U.S. Patent 3761458, 1973. (c) Collete, J. W.; Ro, R. S.; Sonnenberg, F. M. U.S. Patent 3884888, 1975. (d) Collete, J. W.; Ro, R. S.; Sonnenberg, F. M. U.S. Patent 3901860, 1975. (e) Collete, J. W.; Ro, R. S.; Sonnenberg, F. M. U.S. Patent 4017669, 1977. (f) Marie, G.; Lang, A.; Chapelet, G. U.S. Patent 4139417, 1979. (g) Arlt, K. P.; Binsack, R.; Grigo, U.; Neuray, D. U.S. Patent 4423196, 1983. (h) Kawasaki, M.; Minami, S. Jpn. Kokai JO 1-259012-A, 1989.
(12) Polymerization of alkylhalides. (a) Bacskai, R. *J. Polym. Sci., Part A* **1965**, *3*, 2491. (b) Clark, K. J.; Powell, T. *Polymer* **1965**, *6*, 531. (c) Overberger, C. G.; Khattab, G. *J. Polym. Sci., Part A-1* **1969**, *7*, 217.
(13) Datta, S. In *High Value Polymers*; Fawcett, A. H., Ed.; The Royal Society of Chemistry: Cambridge, 1991; pp 33–57.
(14) In many cases the functional group must be precomplexed with 1 equiv of $Al(CH_3)_3$, which results in residual ash in the polymer.
(15) (a) Jordan, R. F.; Bajgur, C. S.; Willett, R.; Scott, B. *J. Am. Chem. Soc.* **1986**, *108*, 7410. (b) Jordan, R. F.; LaPointe, R. E.; Bajgur, C. S.; Echols, S. F.; Willett, R. *J. Am. Chem. Soc.* **1987**, *109*, 4111. (c) Jordan, R. F. *J. Chem. Educ.* **1988**, *65*, 285. (d) Jordan, R. F.; LaPointe, R. E.; Bradley, P. K.; Baenziger, N. *Organometallics* **1989**, *8*, 2892. (e) Jordan, R. F.; LaPointe, R. E.; Baenziger, N.; Hinch, G. D. *Organometallics* **1990**, *9*, 1539.
(16) (a) Turner, H. W.; Hlatky, G. G. Eur. Pat. Appl. 0277003, 1988. (b) Turner, H. W. Eur. Pat. Appl. 0277044, 1988. (c) Hlatky, G. G.; Turner, H. W.; Eckman, R. R. *J. Am. Chem. Soc.* **1989**, *111*, 2728.
(17) (a) Ewen, J. A. Eur. Pat. Appl. 0427697, 1991. (b) Ewen, J. A.; Elder, M. J.; Jones, R. L.; Haspeslagh, L.; Atwood, J. L.; Bott, S. G.; Robinson, K. *Makromol. Chem., Macromol. Symp.* **1991**, *48/49*, 253–295.
(18) (a) Bochman, M.; Wilson, L. M. *J. Chem. Soc., Chem. Commun.* **1986**, 1610. (b) Taube, R.; Krukowka, L. *J. Organomet. Chem.* **1988**, *347*, C9. (c) Bochmann, M.; Jaggar, A. J.; Nicholls, J. C. *Angew. Chem., Int. Ed. Engl.* **1990**, *7*, 780. (d) Eshuis, J. W.; Tan, Y. Y.; Teuben, J. H. *J. Mol. Catal.* **1990**, *62*, 277. (e) Amorose, D. M.; Lee, R. A.; Petersen, J. L. *Organometallics* **1991**, *10*, 2191. (f) Eshuis, J. W.; Tan, Y. Y.; Meetsma, A.; Teuben, J. H.; Renkema, J.; Evens, G. G. *Organometallics* **1992**, *11*, 362–369.
(19) Yang, X.; Stern, C. L.; Marks, T. J. *J. Am. Chem. Soc.* **1991**, *113*, 3623.
(20) Chien, J. C. W.; Tsai, W. M.; Rausch, M. D. *J. Am. Chem. Soc.* **1991**, *113*, 8570.
(21) Related systems will catalyze the polymerization of methacrylates. (a) Zr: Collins, S.; Ward, D. G. *J. Am. Chem. Soc.* **1992**, *114*, 5460. (b) Sm: Yasuda, H.; Yamamoto, H.; Yokota, K.; Miyake, S.; Nakamura, A. *J. Am. Chem. Soc.* **1992**, *114*, 4908.
(22) Allyloxy-*tert*-butyldimethylsilane, (allyloxy)trimethylsilane, 5-TMSO-1-pentene, diallyl ether, diallylphenylamine, and diallyl sulfide did not polymerize under these conditions.
(23) (a) Butler, G. B. *Acc. Chem. Res.* **1982**, *15*, 370. (b) Resconi, L.; Waymouth, R. M. *J. Am. Chem. Soc.* **1990**, *112*, 4953. (c) Coates, G. W.; Waymouth, R. M. *J. Am. Chem. Soc.* **1991**, *113*, 6270. (d) Resconi, L.; Coates, G. W.; Mogstad, A.; Waymouth, R. M. *J. Macromol. Sci., Chem. Ed.* **1991**, *A28*, 1225. (e) Kesti, M. R.; Waymouth, R. M. *J. Am. Chem. Soc.* **1992**, *114*, 3565.
(24) Average activities ±50 turnovers/h; turnover = millimoles of monomer consumed per millimole of Zr.
(25) End-group analysis of the low molecular weight polymers revealed the presence of vinylidene end groups, consistent with β-H elimination.
(26) M_n estimated from ^1H NMR end-group analysis. M_w/M_n determined by GPC analysis. The reaction mixture became quite viscous under these conditions (0.044 mmol of $Cp^*_2HfMe_2$, 0.045 mmol of [*N,N*-dimethylanilinium]$[B(C_6F_5)_4]$, 13.5 mmol of 4-(trimethylsiloxy)-1,6-heptadiene).

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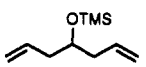
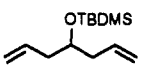
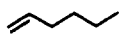
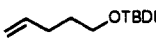
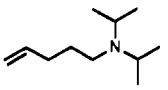
Table I[a]

entry	monomer	metallocene (mmol)	$B(C_6F_5)_3$ (mmol)	temp °C[b]	time (min)	conversn (GC)	turnovers[c]	M_w/M_n[d]	M_n[e]
		$Cp^*_2ZrMe_2$							
1		(0.010)	(0.0050)	22	30	59	280	4.3	920
2		(0.020)	(0.010)	-25	120	98	249	2.7	8100
		(EBTHI)$ZrMe_2$							
3		(0.042)	(0.021)	24	11	81	97	5.3	2900
		$Cp^*_2ZrMe_2$							
4		(0.010)	(0.0049)	22	10	63	324	3.3	670
5		(0.010)	(0.0049)	-25	120	45	209	2.1	11000
		(EBTHI)$ZrMe_2$							
6		(0.010)	(0.0049)	22	10	72	351	3.4	500
7		(0.010)	(0.0049)	-25	120	20	95	1.8	6300
		$Cp^*_2ZrMe_2$							
8		(0.020)	(0.011)	22	30	40	97	2.7	1800
9		(0.020)	(0.011)	-25	120	77	187	2.9	10000
		$Cp^*_2ZrMe_2$							
10		(0.041)	(0.020)	22	60	75	91		2900
11		(0.039)	(0.023)	-25	120	68	78		8800
		(EBTHI)$ZrMe_2$							
12		(0.057)	(0.028)	22	60	72	62		5400

[a] Conditions: A toluene solution of $B(C_6F_5)_3$ was added to a toluene solution of metallocene and 5.0 mmol of monomer; total solution volume = 5 mL. Reactions were monitored by GC. [b] Temperature = ±3 °C. [c] Turnovers = millimoles of monomer consumed per millimole of metallocene. [d] Determined by GPC analysis. GPC analyses of the polyamines were irreproducible. [e] Estimated from ^1H NMR end-group analysis. Cp* = pentamethylcyclopentadienyl, EBTHI = ethylene-1,2-bis(η^5-4,5,6,7-tetrahydro-1-indenyl), TMS = trimethylsilyl, TBDMS = *tert*-butyldimethylsilyl.

derivatives. $[(EBTHI)ZrMe]^+X^-$ catalysts are inactive for the polymerization of 4-TMSO-1,6-heptadiene but readily polymerize the more sterically hindered TBDMS-protected monomer (average activity at 81% conversion = 530 turnovers/h, 88% cyclized by ^1H NMR).

Activities for the polymerization of 5-TBDMSO-1-pentene and 5-(*N*,*N*-diisopropylamino)-1-pentene in the presence of $[Cp^*_2ZrMe]^+X^-$ are lower than that for 1-hexene. Average activities range from 2700 turnovers/h for 1-hexene (44% conversion) to 190 turnovers/h for 5-TBDMSO-1-pentene (40% conversion) to 130 turnovers/h for 5-(*N*,*N*-diisopropylamino)-1-pentene (55% conversion). At least 100 turnovers can be achieved for both functionalized monomers.[27,28] Chiral *rac*-$[(EBTHI)ZrMe]^+X^-$ catalysts are active for the homopolymerization of 1-hexene and 5-(*N*,*N*-diisopropylamino)-1-pentene but not for 5-TBDMSO-1-pentene. Preliminary ^{13}C NMR analyses of polymers obtained in the presence of $[(EBTHI)ZrMe]^+X^-$ are consistent with highly isotactic microstructures.[29]

Treatment of poly(methylene-3,5-(1-TMSO)cyclohexanediyl) with aqueous HCl in hexanes affords the corresponding *polyalcohol* as a white powder (eq 1, 98% yield) which was soluble in DMF, DMSO, and pyridine.[30] Thermogravimetric analysis of this material shows <5% decomposition below 330 °C.[31] Treatment of poly(5-(*N*,*N*-diisopropylamino)-1-pentene) with HCl yields the corresponding poly(ammonium chloride) which is *water soluble* (eq 2).[32]

A major advantage of these metallocene-based catalysts is that the ligand system can be systematically modified to provide the optimal combination of catalytic activity, stereospecificity, and tolerance to functionality. Further studies are underway to extend these results to the synthesis of *optically active, functionalized polyolefins* via enantioselective cyclopolymerization.[23c]

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Supplementary Material Available: Experimental procedures and polymer characterization (8 pages). Ordering information is given on any current masthead page.

(27) In contrast, <50 turnovers were observed for the homopolymerization of functional monomers with $TiCl_3/AlR_3$ catalysts (see refs 7, 9, 11b).

(28) Attempts to directly compare rates for each monomer were frustrated by the sensitivity of the catalyst to impurities. For reproducible results, 5-TBDMSO-1-pentene required approximately 2 times the catalyst concentration and 5-(*N*,*N*-diisopropylamino)-1-pentene required approximately 4 times the catalyst concentration to obtain rates comparable to 1-hexene.

(29) Poly(5-(*N*,*N*-diisopropylamino)-1-pentene): >90% mm dyads. Poly(1-hexene): >90% mm dyads. See: Asakura, T.; Demura, M.; Nishiyama, Y. *Macromolecules* **1991**, *24*, 2334.

(30) Characterized by IR, ^1H and ^{13}C NMR (DMSO-d_6), and elemental analysis.

(31) In contrast, poly(vinyl alcohol) decomposes below 250 °C (see ref 5).

(32) *Polymeric Amines and Ammonium Salts*; Goethals, E. J., Ed.; Pergamon Press; New York, 1980. Characterized by IR, ^1H and ^{13}C NMR ($CDCl_3$), and elemental analysis.

Mechanism of Peptide Release from Major Histocompatibility Complex Class II Molecules

Stephan N. Witt,[†] Brian R. Clark,[‡] and Harden M. McConnell*[,†]

Department of Chemistry
Gilbert Laboratory of Biological Sciences
Stanford University, Stanford, California 94305
Anergen, Inc., 301 Penobscot Drive
Redwood City, California 94063

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Major histocompatibility complex (MHC) class II heterodimeric ($\alpha\beta$) proteins are present as complexes with peptides on the outer plasma membranes of antigen presenting cells.[1] A single MHC class II molecule can bind many different peptides. A significant aspect of the reactions between peptides and solubilized MHC class II molecules is that complexes dissociate slowly ($t_{1/2}$

* Correponding author address: Department of Chemistry, Mudd Chemistry Building 5080, Stanford University, Stanford CA 94305-5080.
[†] Stanford University.
[‡] Anergen, Inc.

(1) Rothbard, J. B.; Gefter, M. L. *Annu. Rev. Immunol.* **1991**, *5*, 477-540.

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