

$\eta^5\text{-C}_5\text{Me}_5\text{TiMe}_2\text{B}(\text{C}_6\text{F}_5)_3$: A Carbocationic Olefin
Polymerization Initiator Masquerading as a
Ziegler–Natta Catalyst

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The utilization of metallocene compounds of titanium, zirconium, and hafnium as homogeneous Ziegler–Natta catalysts for olefin polymerization is well established,¹ and it is recognized that useful catalytic properties generally require the presence of an alkyl ligand, a vacant site, and a positive charge. Thus 16-electron complexes of the type $[\text{Cp}'_2\text{M}(\text{Me})\text{L}]^+$ ($\text{M} = \text{Ti}, \text{Zr}, \text{Hf}$; $\text{Cp}' =$ substituted η^5 -cyclopentadienyl; $\text{Me} =$ methyl; $\text{L} =$ labile ligand) form the most extensively studied class of homogeneous catalysts for the polymerization of olefins. In contrast, although it might be anticipated that 10- and 12-electron complexes of the types $[\text{Cp}'\text{MR}_2]^+$ and $[\text{Cp}'\text{MR}_2\text{L}]^+$ would behave as even more reactive catalysts, for both steric and electronic reasons, there have appeared relatively few publications discussing the utilization of such complexes as olefin polymerization initiators, for the most part for the polymerization of styrene to *syndiotactic* polystyrene (*s*-PS).²

We have shown previously that treatment of Cp^*TiMe_3 ($\text{Cp}^* = \eta^5$ -pentamethylcyclopentadienyl) with $\text{B}(\text{C}_6\text{F}_5)_3$ in toluene results in methyl carbanion abstraction and formation of the arene complex $[\text{Cp}^*\text{TiMe}_2(\eta^6\text{-toluene})][\text{MeB}(\text{C}_6\text{F}_5)_3]$.³ Since the toluene ligand is readily displaced, this complex behaves in solution as a source of the cationic, potentially excellent Ziegler–Natta olefin polymerization catalyst $[\text{Cp}^*\text{TiMe}_2]^+$, and we now describe our preliminary findings on the use of $[\text{Cp}^*\text{TiMe}_2][\text{BMe}(\text{C}_6\text{F}_5)_3]$ to induce polymerization of various olefins. We also provide evidence that this compound can behave as an *initiator* for *carbocationic polymerization*, not solely as a conventional catalyst of Ziegler–Natta processes. Polymerizations of ethylene, propylene, and styrene by $[\text{Cp}^*\text{TiMe}_2][\text{BMe}(\text{C}_6\text{F}_5)_3]$ were briefly described while this work was in progress, but our results differ greatly from those reported elsewhere.^{2b}

We find that bubbling ethylene through solutions of $[\text{Cp}^*\text{TiMe}_2][\text{BMe}(\text{C}_6\text{F}_5)_3]$ (0.03 mmol of Cp^*TiMe_3 , $\text{B}(\text{C}_6\text{F}_5)_3$ in 200 mL

of CH_2Cl_2 , 1,2- $\text{C}_2\text{H}_4\text{Cl}_2$ or toluene) at room temperature results in almost immediate formation of polyethylene (PE) gels containing white, low-solubility polymers with $M_w \geq 300\,000$ and T_m 131–141 °C. While slow monomer diffusion results in low conversions to PE under these conditions, that the catalyst is highly active is attested to by observation that dissolution of Cp^*TiMe_3 and $\text{B}(\text{C}_6\text{F}_5)_3$ in liquid ethylene at –197 °C also results in PE formation; polymerization continues at the boiling point of ethylene (–104 °C). In contrast, the same system is inactive as a catalyst for propylene polymerization (1 atm) at room temperature in toluene, which coordinates to the metal,³ but exhibits mild activity for polymerization of propylene in CH_2Cl_2 and 1,2- $\text{C}_2\text{H}_4\text{Cl}_2$. Small amounts of rubbery, elastomeric polypropylene ($M_w \sim 15,000$, $M_w/M_n \sim 2.1$) are formed and were shown by NMR spectroscopy⁴ to be predominantly syndiotactic polymer (72% *rrrr* pentads).

Treatment of solutions of Cp^*TiMe_3 in styrene with equimolar amounts of $\text{B}(\text{C}_6\text{F}_5)_3$ in toluene (0.03 mmol of Cp^*TiMe_3 in 2.0 mL of styrene, 0.03 mmol of $\text{B}(\text{C}_6\text{F}_5)_3$ in 2.0 mL of toluene) in the temperature range –50 to +70 °C results in significant heating and darkening and almost immediate conversion to solid polystyrene. The product is found to contain small amounts of low molecular weight *s*-PS and atactic polystyrene (*a*-PS) but consists predominantly of high molecular weight *s*-PS (M_w up to 1.7×10^6 , $M_w/M_n = 1.9$ –2.9). After purification of the product,⁵ it is found that overall conversions of monomer to solid *s*-PS are as high as 97% at 40 °C. In contrast, polymerizations run in CH_2Cl_2 or 1,2- $\text{C}_2\text{H}_4\text{Cl}_2$ results only in good yields of *a*-PS.

Our observation that ethylene is polymerized much faster than propylene is consistent with a coordination polymerization mechanism, since the former generally coordinates much more readily than the latter,⁷ but it seemed surprising to find that styrene is polymerized seemingly as rapidly as is ethylene. This relatively sterically demanding olefin should coordinate much less effectively than propylene and, in spite of its higher solubility, might be expected to undergo relatively slow Ziegler–Natta polymerization. However, this aromatic olefin is known to undergo carbocationic polymerization,⁸ and it occurred to us that the strongly electrophilic $[\text{Cp}^*\text{TiMe}_2]^+$ may behave in this case not solely as a conventional Ziegler–Natta catalyst but also as a carbocationic polymerization initiator.⁸

If so, then $[\text{Cp}^*\text{TiMe}_2][\text{BMe}(\text{C}_6\text{F}_5)_3]$ should initiate the polymerization of electron-rich olefins such as *N*-vinylcarbazole and vinyl ethers, which are generally much more susceptible to carbocationic polymerization than is styrene but which do not normally undergo coordination polymerization.^{8,9} Consistent with this hypothesis, we find that addition of Cp^*TiMe_3 and $\text{B}(\text{C}_6\text{F}_5)_3$

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(5) The precipitated polymers were washed well with methanol and dried *in vacuo* at 80 °C. The products were then extracted with acetone. The insoluble *s*-PS was dried at 50 °C for 16 h and purified by dissolution in hot 1,2,4-trichlorobenzene, followed by precipitation with acidified methanol. Tacticity of the *s*-PS was assessed by $^{13}\text{C}\{^1\text{H}\}$ NMR spectroscopy on solutions in 1,1,2,2-tetrachloroethane-*d*₂ at 120 °C, the resonances of the *ipso*-carbon atoms being well-resolved singlets at δ 145.36, characteristic of the *rrrr* pentad of *s*-PS.⁶

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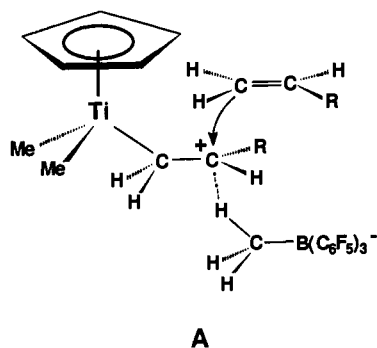
(8) (a) Kennedy, J. P.; Maréchal, E. *Carbocationic Polymerization*; John Wiley and Sons: New York, 1982. (b) Kennedy, J. P.; Iván, B. *Designed Polymers by Carbocationic Macromolecular Engineering: Theory and Practice*; Hanser Publishers: Munich, FRG, 1991. (c) Sawamoto, M. *Prog. Polym. Sci.* **1991**, *16*, 111.

(1) See, for instance: (a) Keii, T.; Soga, K., Eds. *Catalytic Polymerization of Olefins*; Elsevier: New York, 1986. (b) Kaminsky, W.; Sinn, H., Eds. *Transition Metals and Organometallics as Catalysts for Olefin Polymerization*; Springer-Verlag: Berlin, 1988. (c) Quirk, R. P., Ed. *Transition Metal Catalyzed Polymerizations; Ziegler–Natta and Metathesis Polymerizations*; Cambridge University Press: Cambridge, U.K., 1988. See also: Jordan, R. F. *Adv. Organomet. Chem.* **1991**, *32*, 325.

(2) See, for instance: (a) Chien, J. C. W.; Salajka, Z. *J. Polym. Sci.: Part A* **1991**, *29*, 1253. (b) Pellechia, C.; Longo, P.; Proto, A.; Zambelli, A. *Makromol. Chem., Rapid Commun.* **1992**, *13*, 265. (c) Kucht, A.; Kucht, H.; Barry, S.; Chien, J. C. W.; Rausch, M. D. *Organometallics* **1993**, *12*, 3075. For representative, recent patents describing catalyst systems similar to those described here, see: (d) Takeuchi, M.; Kuramoto, M. (Idemitsu Kosan Co., Tokyo, Japan). U.S. Patent 5,023,304, June 11, 1991. (e) Campbell, R. E. (The Dow Chemical Co., Midland, MI). U.S. Patent 5,066,741, Nov 19, 1991. (f) Canich, J. A. M. (Exxon Chemical Patents, Inc., Linden, NJ). U.S. Patent 5,096,867, March 17, 1992. (g) Stevens, J. C.; Neithamer, D. R. (The Dow Chemical Co., Midland, MI). U.S. Patent 5,132,380, July 21, 1992.

to the liquid vinyl ethers CHR=CHOR' (R = H, Me; R' = Me, Et, *i*-Bu), 2,3-dihydrofuran, and 3,4-dihydro-2*H*-pyran or to solutions of these or of *N*-vinylcarbazole in CH₂Cl₂ or toluene at -78 or +20 °C results in rapid heating and formation of the corresponding polymers. For most of the vinyl ether polymers, $M_w = 10^4$ - 10^5 and $M_w/M_n = 1.1$ -2.8, properties comparable with those of polymers formed by the better carbocationic polymerization initiators described previously.^{9a} We note that poly(3,4-dihydro-2*H*-pyran), for which $M_w \approx 10^3$, $M_w/M_n = 1.38$ -2.08, seems heretofore not to have been reported; only oligomers have been formed in earlier work.^{9d} For *N*-vinylcarbazole, as well, unusually high molecular weight polymer ($M_w \approx 10^5$, $M_w/M_n = 3.5$)^{9b} was obtained. The relatively narrow molecular weight dispersions obtained in all cases are typical of carbocationic polymerization processes.⁸

It is likely that polymerization would be initiated as suggested in A, where the carbocationic center of a metal ion-activated olefin is being attacked by a second monomer in the manner normally proposed for carbocationic polymerization processes.⁸



A

Here the olefin-metal interaction would involve a nonclassical η^1 - rather than the conventional mode of η^2 -bonding, and we note that this mode of bonding is approximated in ground-state structures of vinyl alcohol, ether, and amine complexes of electrophilic metals.¹⁰

Further evidence for carbocationic initiation in these systems is provided by molecular weight distributions and end group analyses of the products formed when polymerizations are quenched with alcohols. If, for instance, styrene were polymerized by a Ziegler-Natta process, alcoholysis of a growing polymer chain should result in a saturated oligomer backbone with a methyl group at one end and a benzyl group at the other.⁷ On the other hand, alcoholysis of the growing chain of A should result in a methyl group at one end and an *alkoxy* group at the other. NMR analysis of the polystyrene obtained from a reaction in toluene

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at 0 °C but quenched immediately after initiation with *tert*-butyl alcohol shows unambiguously that the *s*-PS fraction does indeed contain a *tert*-butoxy end group (¹H NMR δ 2.12; ¹³C{¹H} NMR δ 31.1). Also in accord with a carbocationic mechanism,⁸ we find for this material that $M_w \approx 50\,000$, considerably lower than that obtained under conditions where chain growth is not terminated prematurely. Similar quenching of an ethyl vinyl ether polymerization reaction with aqueous methanol should result in the formation of polymer containing an aldehyde group, the product of hydrolysis of the expected acetal group. An aldehydic resonance at δ 9.9 in the ¹H NMR spectrum of the product was indeed observed, as has been noted for a very similar system.¹¹

The implications of these conclusions for the mechanism(s) of polymerization of styrene to *s*-PS by other putative Ziegler-Natta catalyst systems² are not yet clear, and it is possible that both Ziegler-Natta and cationic processes pertain with different polymerization initiators. Indeed, the fact that some low molecular weight *s*-PS is formed by [Cp*TiMe₂][BMe(C₆F₅)₃] may provide evidence for a Ziegler-Natta route, thereby relating this initiator to apparently similar systems reported previously.² While experiments involving isotopic labeling and end group analyses have been interpreted in terms of a coordination polymerization mechanism in which monomer insertion is secondary and involves *cis*-addition of the growing chain to the olefin, with the stereochemistry of addition under chain end control,^{6b,12} one can demonstrate that the data are equally consistent with a carbocationic mechanism for chain growth and termination.

Finally, inasmuch as cationic polymerization of styrene normally yields soluble PS which seems generally assumed to be atactic,⁸ our finding of stereoregular polystyrene growth may seem incompatible with the postulated cationic process. However, α -methylstyrene and vinyl ethers can be polymerized stereoselectively via carbocationic processes,¹³ in which ion pairing of the counteranion with the nascent carbocationic center plays an important albeit not well understood role.⁸ Furthermore, since the BMe(C₆F₅)₃⁻ counterion is chiral, strong ion pairing could well result in the introduction of a degree of enantioselectivity which is not possible with the commoner achiral counterions. Support for this suggestion is found in the relatively low proportions of *s*-PS obtained in more polar solvents, a result which may be rationalized on the basis of decreased ion pairing in these media.

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