Communications to the Editor

η^5-$C_5Me_5TiMe_3$−$B(C_6F_5)_3$: A True Ziegler−Natta Catalyst for the Syndiotactic-Specific Polymerization of Styrene

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The development of homogeneous Ziegler−Natta catalysts has provided synthetic routes to polymers having novel structures.[1] Among them, syndiotactic polystyrene (s-PS), first synthesized in 1986 by Ishihara *et al.*,[2] has attracted much interest for its properties and potential applications.[1] Suitable catalytic systems producing s-PS can be obtained from many different Ti and a few Zr compounds by activation with a large excess of methylalumoxane (MAO), half-titanocenes of the type $Cp'TiX_n$ (Cp' = substituted or unsubstituted η^5-cyclopentadienyl; X = halogen, alkoxy, or hydrocarbyl, n = 2, 3) affording the most efficient catalysts.[3] Many features of the polymerization mechanism have been elucidated.[4] In particular, a Ziegler−Natta mechanism involving secondary monomer insertion into the metal−carbon bonds of the active species has been assessed on the basis of several experimental findings, the strongest evidence arising from the observation by NMR analysis of ^{13}C-enriched ···$CH(Ph)CH_2{}^{13}CH_2CH_3$ end groups in a s-PS sample prepared in the presence of the catalytic system $Ti(CH_2Ph)_4$−MAO−$Al(^{13}CH_2CH_3)_3$.[4a]

Later on, we described[5] novel MAO-free catalysts based on Cp^*TiR_3 (Cp^* = η^5-C_5Me_5, R = Me or CH_2Ph) activated with 1 equiv of $B(C_6F_5)_3$, which are highly active for the polymerization of ethylene and propylene[5a] and the syndiospecific polymerization of styrene,[5b] and suggested the formation of cationic active species.[4e,5−7] More recently, Baird *et al.*[8] also reported the use of the title catalyst for the polymerization of ethylene, styrene, and electron-rich olefins, such as *N*-vinylcarbazole and vinyl ethers. On the basis of the latter finding and the observation of NMR resonances attributed to the presence of a *tert*-butoxy end group in a s-PS sample quenched with *tert*-butyl alcohol, they proposed a carbocationic mechanism for the syndiospecific polymerization of styrene *at least* in the presence of Cp^*TiMe_3−$B(C_6F_5)_3$. While it is not surprising that electrophilic species formed in this system may function as carbocationic polymerization initiators toward electron-rich monomers, it seemed unlikely to us that such different pathways as Ziegler−Natta and carbocationic polymerization mechanisms could be operative in MAO-based and MAO-free catalysts affording s-PS having indistinguishable structures.

In order to discriminate between the two mechanisms, we have investigated the syndiospecific polymerization of styrene in the presence of the title catalyst, and in particular the initiation and termination steps.

Thus, a polymerization run[9] has been carried out by using Cp^*TiMe_3 premixed with ~1.5 equiv of 75%-^{13}C-enriched $Al(CH_3)_3$ (under these conditions, NMR monitoring shows fast methyl exchange between Ti and Al and no significant side reaction) and then activated with 1 equiv of $B(C_6F_5)_3$. The obtained polystyrene was extracted with boiling 2-butanone: the ^{13}C NMR spectrum of the insoluble fraction (90%), recorded in $C_2D_2Cl_4$ at 120 °C, shows, in addition to the resonances attributable to the backbone carbons of highly syndiotactic polystyrene,[2,3] a resonance at 9.8 ppm from hexamethyldisiloxane. This resonance, which is absent in samples prepared with the title catalyst under similar conditions, but adding unenriched $Al(CH_3)_3$ or no $Al(CH_3)_3$ at all, is attributed to the ^{13}C-enriched ···$CH(Ph)CH_2{}^{13}CH_3$ end groups, by comparison with a resonance previously observed in a polystyrene sample prepared with a ^{13}C-enriched heterogeneous Ziegler−Natta catalyst.[10] The mentioned end groups can only reasonably arise from the initiation step by secondary insertion of styrene into the Ti−$^{13}CH_3$ bond of the active species (eq 1), generated by methyl exchange between Al and Ti.[11]

$$\mathrm{Ti^{13}CH_3} \xrightarrow[\text{2,1 insertion}]{\mathrm{CH_2{=}CHPh}} \mathrm{TiCH(Ph)CH_2{}^{13}CH_3} \xrightarrow[\text{2,1 insertion}]{n\,\mathrm{CH_2{=}CHPh}} \mathrm{Ti(CH(Ph)CH_2)}_n\mathrm{CH(Ph)CH_2{}^{13}CH_3} \quad (1)$$

In order to ascertain the possibility of incorporation of alkoxy end groups in the termination step, as proposed by Baird *et al.*,[8]

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(1) See, for instance: Soga, K., Terano, M., Eds. *Catalyst Design for Tailor-Made Polyolefins*; Kodansha: Tokyo, 1994.

(2) Ishihara, N.; Seimiya, T.; Kuramoto, M.; Uoi, M. *Macromolecules* **1986**, *19*, 2464.

(3) (a) Grassi, A.; Pellecchia, C.; Longo, P.; Zambelli, A. *Gazz. Chim. Ital.* **1987**, *117*, 65. (b) Kakugo, M.; Miyatake, T.; Mizunuma, K. *Chem. Express* **1987**, *2*, 445. (c) Ishihara, N.; Kuramoto, M.; Uoi, M. *Macromolecules* **1988**, *21*, 3356. (d) Zambelli, A.; Oliva, L.; Pellecchia, C. *Macromolecules* **1989**, *22*, 2129.

(4) (a) Pellecchia, C.; Longo, P.; Grassi, A.; Ammendola, P.; Zambelli, A. *Makromol. Chem., Rapid Commun.* **1987**, *8*, 277. (b) Zambelli, A.; Longo, P.; Pellecchia, C.; Grassi, A. *Macromolecules* **1987**, *20*, 2035. (c) Longo, P.; Grassi, A.; Proto, A.; Ammendola, P. *Macromolecules* **1988**, *21*, 24. (d) Chien, J. C. W.; Salajka, Z. *J. Polym. Sci., Part A: Polym. Chem.* **1991**, *29*, 1243, 1253. (e) Zambelli, A.; Pellecchia, C.; Oliva, L.; Longo, P.; Grassi, A. *Makromol. Chem.* **1991**, *192*, 223.

(5) (a) Pellecchia, C.; Proto, A.; Longo, P.; Zambelli, A. *Makromol. Chem., Rapid Commun.* **1992**, *13*, 277. (b) Pellecchia, C.; Longo, P.; Proto, A.; Zambelli, A. *Makromol. Chem., Rapid Commun.* **1992**, *13*, 265.

(6) Cationic complexes of the type $[Cp_2MR]^+$ are commonly implicated as the active species in metallocene-based Ziegler−Natta catalysts. See, e.g.: (a) Jordan, R. F. *Adv. Organomet. Chem.* **1991**, *32*, 325 and references therein. (b) Marks, T. J. *Acc. Chem. Res.* **1992**, *25*, 57.

(7) Cationic Ti and Zr monocyclopentadienyl derivatives have been also synthesized by reaction of Cp^*MR_3 and $B(C_6F_5)_3$: (a) Gillis, D. J.; Tudoret, M.-J.; Baird, M. C. *J. Am. Chem. Soc.* **1993**, *115*, 2543. (b) Pellecchia, C.; Immirzi, A.; Grassi, A.; Zambelli, A. *Organometallics* **1993**, *12*, 4473. There is experimental evidence, however, that the initially formed $[Cp^*TiR_2]^+$ complexes rapidly decompose to Ti(III) species, which are probably the true catalytic species for the syndiospecific polymerization of styrene: (c) Zambelli, A.; Pellecchia, C.; Proto, A. *Macromol. Symp.* **1995**, *89*, 373. (d) Grassi, A.; Pellecchia, C.; Oliva, L.; Laschi, F. *Macromol. Chem. Phys.* **1995**, *196*, 1093.

(8) Quyoum, R.; Wang, Q.; Tudoret, M.-J.; Baird, M. C.; Gillis, D. J. *J. Am. Chem. Soc.* **1994**, *116*, 6435.

(9) Cp^*TiMe_3 (0.088 mmol) dissolved in 2 mL of toluene was mixed with 0.12 mmol of 75%-^{13}C-enriched $Al(CH_3)_3$ and then with $B(C_6F_5)_3$ (0.088 mmol) in 2 mL of toluene; styrene (1.5 mL) was added at 18 °C. The polymerization was terminated after 10 min with acidified methanol. The polymer was washed with fresh methanol, recovered by filtration, and dried *in vacuo* at 90 °C for 12 h. Yield: 80 mg. The polymer was then extracted in a Kumagawa extractor with boiling 2-butanone, and the insoluble fraction was washed with methanol and dried *in vacuo* at 90 °C.

(10) Ammendola, P.; Tancredi, T.; Zambelli, A. *Macromolecules* **1986**, *19*, 307. In the latter paper, the assignment was made on the basis of a discrete model compound reported in the literature: Sato, H.; Tanaka, Y. In *NMR and Macromolecules*; Randall, J. C., Ed.; ACS Symposium Series 247, American Chemical Society: Washington, DC, 1984; p 181.

(11) NMR analysis of a s-PS sample prepared in the presence of $Cp^*Ti(^{13}CH_3)_3$−$B(C_6F_5)_3$ without addition of any $Al(CH_3)_3$ also showed the mentioned resonance at 9.8 ppm.

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a polymerization run[12] carried out in the presence of Cp*$TiMe_3$–$B(C_6F_5)_3$ was terminated soon after initiation with 99%-^{13}C-enriched CH_3OH. In the ^{13}C NMR spectrum of the obtained s-PS fraction no resonance attributable to $^{13}CH_3O$ ··· end groups was detected. In another experiment,[13] a polymerization run performed in the presence of Cp*$TiMe_3$–$Al(^{13}CH_3)_3$–$B(C_6F_5)_3$ (1:1:1 molar ratio) was terminated after 30 s with $^{13}CH_3OH$: the ^{13}C NMR spectrum (see Figure 1) of the obtained s-PS does contain an intense resonance at 9.8 ppm due to the ··· CH(Ph)-$CH_2{}^{13}CH_3$ end group formed in the initiation step, but does not contain resonances attributable to end groups formed in the termination step. Similarly, several polymerization runs performed with Cp*$TiMe_3$–$B(C_6F_5)_3$ at temperatures ranging between −10 and 25 °C and reaction times ranging between 10 and 300 s were terminated with *tert*-butyl alcohol: in any case, the ^1H and ^{13}C NMR spectra of the s-PS fractions, thoroughly washed with methanol and dried *in vacuo* at 90 °C, did not contain resonances attributable to *tert*-butoxy end groups.[14]

The incorporation of ^{13}C-enriched end groups in polymer samples produced in the presence of ^{13}C-enriched catalytic systems and the lack of incorporation of alkoxy end groups when growing polymer chains are terminated by alcoholysis are fully consistent with a Ziegler–Natta mechanism, while they are incompatible with any carbocationic polymerization mechanism.

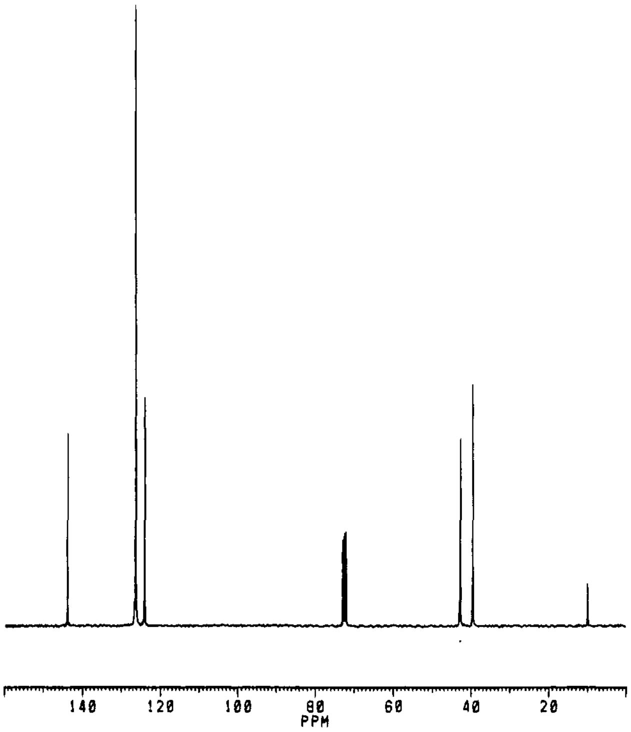

Figure 1. ^{13}C NMR spectrum of a s-PS sample obtained in a polymerization run promoted by Cp*$TiMe_3$–$Al(^{13}CH_3)_3$–$B(C_6F_5)_3$ and terminated by $^{13}CH_3OH$: δ in ppm from hexamethyldisiloxane.

In conclusion, investigation of the initiation and termination steps in syndiotactic-specific polymerization of styrene strongly implicates the occurrence of a Ziegler–Natta (i.e., polyinsertion) mechanism even in the presence of the catalytic system Cp*$TiMe_3$–$B(C_6F_5)_3$, as previously shown for closely related systems based on methylalumoxane, which reasonably involve analogous active species. In contrast to a previous report,[8] no evidence supporting a carbocation mechanism is found by alcoholysis of growing chains.

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(12) This run was carried out as described in ref 9, by using Cp*$TiMe_3$, 0.044 mmol; $B(C_6F_5)_3$, 0.044 mmol; toluene, 5 mL; and styrene, 2 mL. The run was terminated after 50 s with 0.5 mL of 99%-^{13}C-enriched CH_3OH (Aldrich, dried over 3 Å molecular sieves), and the polymer (55 mg) was worked up as above.

(13) This run was carried out as described in ref 9, by using Cp*$TiMe_3$, 0.13 mmol; $Al(^{13}CH_3)_3$, 0.13 mmol; $B(C_6F_5)_3$, 0.13 mmol; toluene, 3 mL; and styrene, 2 mL. The run was terminated after 30 s with 0.5 mL of $^{13}CH_3OH$, and the polymer (60 mg) was worked up as above.

(14) Indeed, when the polystyrene samples are extracted with boiling acetone and the insoluble fractions (which still contain some stereoirregular polymer) are dried at temperatures lower than 70 °C, resonances are found at 2.04 ppm in the ^1H and at 28.6 ppm in the ^{13}C NMR spectra (from hexamethyldisiloxane, used as internal chemical shift reference at 120 °C): these resonances, which disappear after prolonged drying at 90 °C under reduced pressure, are due to residual acetone in the samples. In ref 8, resonances at 2.12 ppm in the ^1H and 31.1 ppm in the ^{13}C NMR spectra (TMS scale) were attributed to *tert*-butoxy end groups. We note that these resonances are almost coincident within the experimental error with the above mentioned acetone resonances, by considering that at 120 °C $\delta_{(HMDS)} - \delta_{(TMS)} = -0.05$ ppm for ^1H and −2.1 ppm for ^{13}C. Moreover the methyl ^1H resonances of *tert*-butyl ethers are usually found about 1 ppm upfield: see, e.g., *The Aldrich Library of ^{13}C and ^1H NMR FT NMR Spectra*, Edition I; Aldrich Chemical Co.: Milwaukee, WI, 1993. It is also worth recalling that s-PS is known to strongly retain a variety of solvents; see, e.g.: Immirzi, A.; de Candia, F.; Iannelli, P.; Vittoria, V.; Zambelli, A. *Makromol. Chem., Rapid. Commun.* **1988**, *9*, 761.