

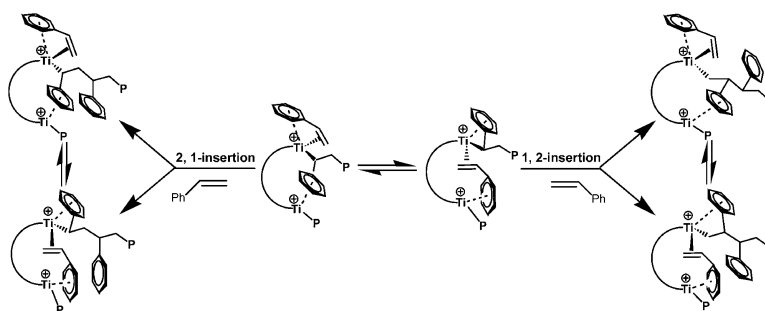
Communication

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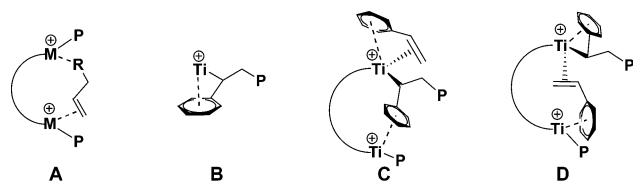
Bimetallic Catalysis for Styrene Homopolymerization and Ethylene–Styrene Copolymerization. Exceptional Comonomer Selectivity and Insertion Regiochemistry

Neng Guo, Liting Li, and Tobin J. Marks*

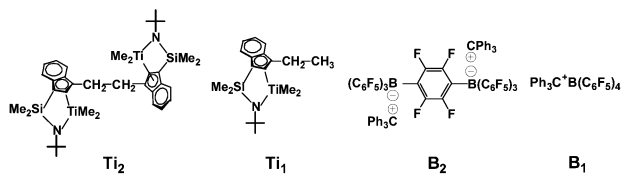
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Over the past few decades, ethylene–styrene copolymers have received great attention due to their impressive viscoelastic behavior, mechanical properties, and compatibilities with other polymeric materials.¹ Previous attempts to copolymerize ethylene and styrene via free radical or heterogeneous Ziegler–Natta processes have proven largely unsuccessful, typically yielding homopolymer mixtures or copolymers with styrene incorporation <1 mol %.² The development of homogeneous single-site polymerization catalysts led to a resurgence of interest in this field;^{3,5} however, challenges remain. For Cp'TiXYZ-type catalysts (Cp' = substituted or unsubstituted cyclopentadienyl; X, Y, Z = Cl, alkyl, alkoxy, etc. ligand),³ substantial quantities of homopolymer contaminants are coproduced in addition to ethylene–styrene copolymers, likely due to multiple active species. *Ansa*-amido-monocyclopentadienyl Ti and Zr constrained geometry catalysts (CGCs)⁴ produce ethylene–styrene copolymers exclusively; however, styrene incorporation is invariably <50 mol %, regardless of the styrene:ethylene feed ratio.⁵ We recently demonstrated that, compared to monometallic CGCs, bimetallic variants incorporate far greater quantities of aliphatic α -olefin comonomers during ethylene copolymerizations, including sterically encumbered isobutene.⁶ It was speculated that the dicationic bimetallic framework exhibits enhanced comonomer binding affinity/activating capacity (e.g., **A**). Since styrene has potentially coordinating alkenyl and aromatic π -electron regions, we envisioned that bimetallic CGC catalysts might mediate unusual styrene polymerization patterns. We report here that binuclear **Ti**₂



not only exhibits far greater activity for styrene homopolymerization than does **Ti**₁, but affords broad-range controllable styrene incorporation in ethylene–styrene copolymerizations. Multinuclear



cooperative effects are substantial and include modification of enchainment regiochemistry.

All polymerizations were carried out under rigorous exclusion of O₂, moisture, and impurities.⁷ The results of styrene homopolymerization experiments (Table 1) reveal striking cocatalyst-

Table 1. Styrene Homopolymerization Results^a

entry	cat. + cocat.	time (h)	yield (g)	act ^b ($\times 10^4$)	T_g^c (°C)	T_m^c (°C)	M_w^e ($\times 10^4$)	M_w/M_n^e
1	Ti ₁ + B ₁	3	0.08	0.27	104.6	n.o. ^d	1.96	1.86
2	Ti ₂ + B ₁	3	3.13	10.43	96.4	n.o. ^d	1.04	1.55
3	Ti ₁ + B ₂	3	0.06	0.20	100.5	n.o. ^d	1.21	1.69
4	Ti ₂ + B ₂	3	3.36	11.20	89.2	n.o. ^d	0.80	1.47

^a [Ti] = 10 μ mol + [B] = 10 μ mol, 5 mL of styrene + 25 mL of toluene at 20 °C. ^b Units: g polymer/(mol Ti \times atm \times h). ^c DSC. ^d Not observed. ^e GPC relative to polystyrene standards.

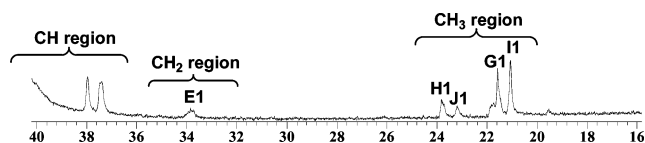
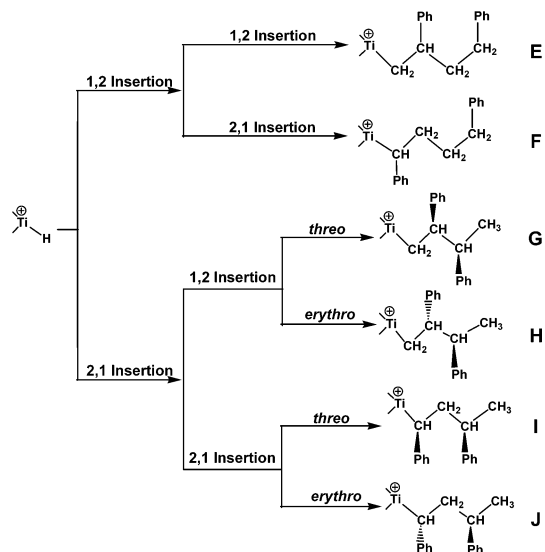


Figure 1. ¹³C NMR end group analysis of sample 2 from Table 1 (100 MHz) in 1:1 volume of 1,2,4-trichlorobenzene (containing 0.1 M Cr(acac)₃)/1,1,2,2-tetrachloroethane-*d*₂.

independent differences between **Ti**₂ and **Ti**₁. Under identical conditions, **Ti**₁ produces only trace quantities of styrene homopolymer whereas **Ti**₂ activated by either **B**₁ or **B**₂ exhibits significantly higher homopolymerization activity. All product polymers (entries 1–4) exhibit a single endothermic DSC feature between 89 and 113 °C, the characteristic glass transition temperature (T_g) region of atactic polystyrene. ¹³C NMR also demonstrates the polymers to be atactic. More importantly, monomodal GPC traces with polydispersities \sim 2 and end group analyses show that all the polystyrene homopolymers are produced exclusively via a coordinative/insertive pathway. The low styrene homopolymerization activity of **Ti**₁ is consistent with earlier results,^{5c} and is thought to reflect deactivation via intramolecular arene coordination in the 2,1-insertion product (e.g., **B**).⁸ In contrast to this picture, we suggest that for bimetallic **Ti**₂, the arene ring of the last inserted styrene may preferentially coordinate to the adjacent Ti center, reducing coordinative saturation at the polymerization site and accelerating homopolymerization.⁹ The coordinated arene rings can in principle participate in several types of multimetallic/enchainment-altering interaction. For example, structure **C** depicts an η^n, η^2 motif in which styrene interacts with a single Ti center while the phenyl group of the last inserted styrene interacts with the second Ti.¹⁰ As depicted, structure **C** formally favors 2,1-styrene insertion, while structure **D** formally favors 1,2-insertion. Scheme 1 depicts all possible end groups produced during the initiation steps in styrene homopolymerization. All structures except **F** are found in the ¹³C NMR end group analysis (Figure 1) of the present homopolymers.¹¹ The relative spectral intensities indicate that 1,2-insertion competes with 2,1-insertion to a significant degree *only in the bimetallic system*, arguing that this unusual insertion regiochemistry¹² arises from the unique catalyst structure.

Scheme 1. Possible Styrene Insertion Pathways during Initiation**Table 2.** Styrene and Ethylene Copolymerization Catalyzed by $Ti_2 + B_1$ ^a

entry	S/T (mL/mL)	time (h)	yield (g)	act ^b ($\times 10^5$)	T_g^c ($^{\circ}C$)	M_w^d ($\times 10^3$)	M_w/M_n	styrene% ^e
5	10/50	1.0	2.59	2.59	21.7	3.58	1.82	39
6	20/40	1.5	2.91	1.94	31.4	4.71	1.33	50
7	30/30	0.5	1.92	3.84	35.8	4.38	2.40	66
8	60/0	0.5	1.56	3.12	39.6	4.79	1.72	76

^a Ti_2 (5 μ mol) + B_1 (10 μ mol) at 20 $^{\circ}C$, under 1.0 atm ethylene pressure. S = styrene, T = toluene. ^b Units: g polymer/(mol Ti \times atm \times h). ^c DSC. ^d T_m not observed. ^e GPC relative to polystyrene standards. ^f From ^{13}C NMR (see refs 3d and 11 for the assay procedure).

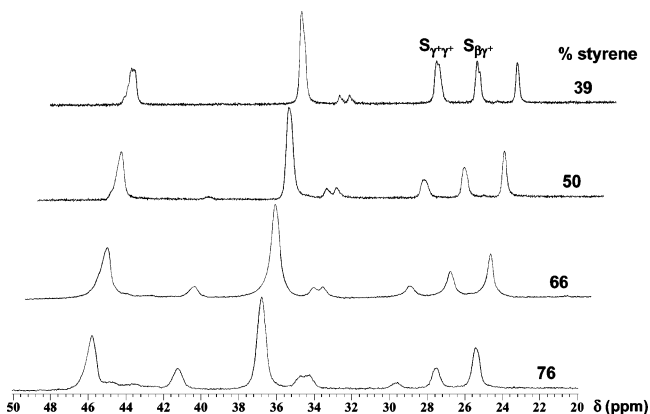
**Figure 2.** Aliphatic region ^{13}C NMR spectra of styrene and ethylene copolymers from Table 2 (100 MHz) in 1:1 volume of 1,2,4-trichlorobenzene (containing 0.1 M $Cr(acac)_3/1,1,2,2$ -tetrachloroethane- d_2).

Table 2 summarizes ethylene–styrene copolymerization results. All polymers exhibit a single endothermic feature in the DSC, which falls within the T_g range reported for ethylene–styrene copolymers with similar monomer contents.^{1c} GPC traces are all monomodal, consistent with the predominance of a single homogeneous catalytic species. Solvent fractionation^{3c} experiments reveal negligible quantities of homopolymer impurities. Thus, all evidence indicates that the polymers produced by the bimetallic catalyst are exclusively ethylene–styrene copolymers. ^{13}C NMR spectra of the copolymers produced by Ti_2 vs. Ti_1 activated with B_1 or B_2 and run to constant conversion clearly show, for the same cocatalyst, that Ti_2 incorporates $\sim 20\%$ more styrene than Ti_1 .⁷

Table 2 and Figure 2 show that with increasing styrene/ethylene feed ratio, copolymers produced by $Ti_2 + B_1$ have progressively

higher styrene incorporation, up to 76%.¹³ When styrene incorporation is $> 50\%$, at least three consecutive head-to-tail coupled styrene units are observed in addition to tail-to-tail coupled dyads.^{3a,c,14} This result contrasts conventional mononuclear CGC catalysts, which incorporate a maximum of 50% styrene, regardless of the feed ratio, and where, of the three possible dyads, only tail-to-tail coupling is observed.^{5c}

The present binuclear organotitanium catalyst not only effects styrene homopolymerization with high activity, but also is the first catalyst that can produce ethylene–styrene copolymers with broad-range control of styrene enchainment. Further ramifications of the proposed mechanism are under investigation.

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Supporting Information Available: Detailed experimental procedures and copolymer ^{13}C NMR data (PDF). This material is available free of charge via the Internet at <http://pubs.acs.org>.

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